Volume X. *April, 1900.* *Number 4.*

THE

PHYSICAL REVIEW.

THE ACOUSTIC ANALYSIS OF THE VOWELS FROM THE PHONOGRAPHIC RECORD.

By Louis Bevier, Jr.

THE use of the phonograph in the scientific study of vowel timbre is not new. It began more than twenty years ago when the instrument was still in an undeveloped stage, and much less true to timbre than it is today. One difficulty has been to secure a sufficiently magnified trace of the record for convenient study. The apparatus of Jenkin and Ewing[1] magnified ordinates 400 times, but was a machine of some complexity, and too delicate for general use by investigators. Its records, except in the hands of laboratory experts, would be untrustworthy.

Since that time many attempts have been made with more or less success, but I know of no apparatus so simple and inexpensive as that by means of which I have obtained, with the aid of my colleague, Dr. F. C. Van Dyck, Professor of Physics in Rutgers College, vowel-curves of very great clearness, and in which the ordinates are magnified about 1000 times. Moreover, the mere substitution of a different lens makes it possible to magnify as much more as may be desired, certainly up to 5000 times without much difficulty.

The apparatus used is illustrated diagrammatically in figure 1, page 194, which shows all the essential parts. We took an Edison automatic reproducer, such as is regularly sold with the machines, removed the diaphragm, and fastened to the tracing lever

[1] Transactions of the Royal Society of Edinburgh, 1878.

a rigid arm bearing an adjustable plane mirror. A spring, fastened to this arm, holds the sapphire knob of the reproducer lightly but firmly in the furrow of the wax. It should be just stiff enough to raise the weight of the movable plate, on which the lever is mounted,

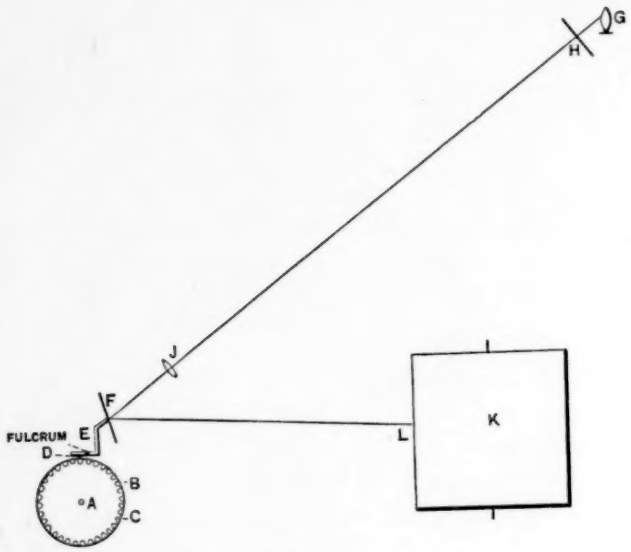


Fig. 1.

A = section of phonograph wax cylinder.
B = surface of the wax.
C = bottom of the furrow, with undulations much exaggerated.
D = sapphire knob of tracer.
E = rigid lever bearing adjustable mirror.
F = adjustable plane mirror.
G = source of light.
H = plate with pin hole through which light passes.
J = convex lens with conjugate foci at *H* and *L*.
K = revolving drum carrying bromide paper.
L = surface of paper on which point of light leaves the sinuous trace.

and press the whole snugly up against the carriage frame, in order that not the smallest movement of the knob can be taken up at bearings, but that every movement, small or great, shall be faithfully imparted to the mirror. Then a narrow beam of light reflected from the mirror and focused on moving bromide paper will leave a sinuous trace exactly corresponding to the profile of the bottom of the furrow in the wax. The magnifying power of this arrangement is very great, because the long arm of the lever is a beam of light, and making this arm longer is for the most part a very simple matter. To magnify 400 times by a system of material

levers without falsifying the record by various accidental tremors was a matter of great difficulty, whereas by this plan it would be quite easy to magnify as much as 5000 times, if such enlargement should be found desirable. In my machine the distance from the sapphire knob to the fulcrum is about one-eighth of an inch, hence when the other arm is only ten feet we have magnified already nearly 1000 times. Thus far I have been content with this result, but have used a longer arm in a few experiments and found no new difficulties introduced. Making the short arm one-sixteenth of an inch, and working with a beam of light thirty feet in length would obviously magnify more than 5000 times. The chief difficulty would be to secure a fine point of light at so great a focal distance.

Besides this tracer one must have a good motor to turn the drum on which the bromide paper is carried. This should be adjustable, and as uniform in motion as possible, for if the drum does not revolve uniformly, the abscissas will be hopelessly falsified. Another motor also is needed which will give to the wax cylinder a very slow and uniform motion of rotation. When these preliminaries are arranged and the whole is installed in a room sufficiently dark for photographic work the difficulties of manipulation are not great. I may briefly describe the necessary steps. After the sound which it is desired to study has been sung into the instrument, and the sound-waves are thus recorded on the wax cylinder in the usual way, an ordinary reproducer should be placed in the carriage and a test be made to ascertain whether the instrument gives back the sound with truth and precision. One learns by a little practice to make records which come back with great perfectness of timbre, and this is most important if our results are to have permanent value. A record thus tested by reproduction is now ready to be transcribed. Remove the reproducer and insert in its place the transcriber already explained, adjusting carefully so that the knob runs precisely in the bottom of the furrow. Arrange the light so as to get as small and as perfect a point as possible on the drum. Place the bromide paper on the drum and start the two motors. The point of light will move up and down on the bromide paper, and as the drum revolves a sinuous line is recorded which becomes visible at once when the paper is treated with a developer. The drum

should be so adjusted that as it revolves it will move either up or down on its axis so that the trace will not come round into itself. This may be done by hand, but it is better to have an automatic device such as can be arranged in any laboratory. On a strip of paper two feet long and six inches wide we may obtain a sinuous trace in this way of twelve feet or more, according to the amount of axial motion given to the drum with each revolution.

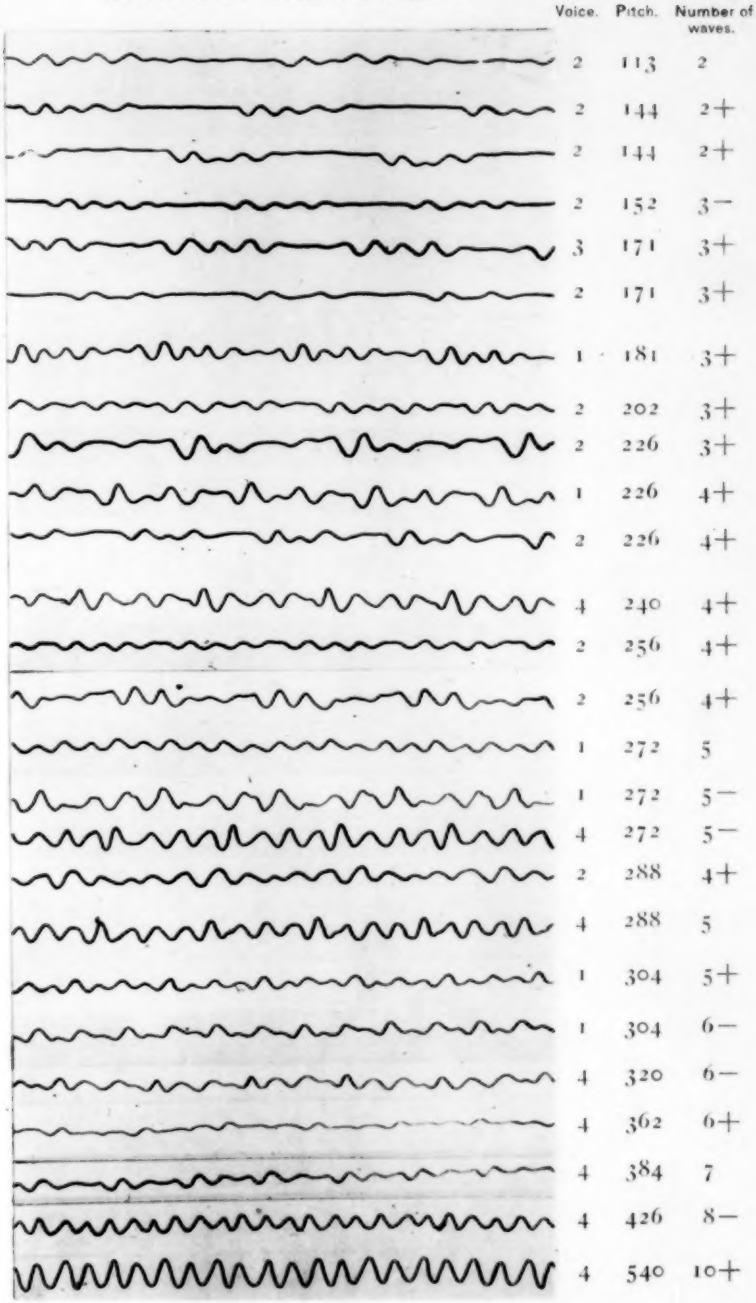
The actual depth of the hollows in the records carried by the wax cylinder is seldom more than 1/2000 of an inch, and generally very much less, so that when ordinates are magnified 1000 times the apparent amplitude as shown in the trace is seldom more and generally less than one-half an inch. An apparent amplitude of one half an inch makes a very loud sound in reproduction, and even when the greatest apparent amplitude is one-tenth of an inch the sound heard in reproduction is very clear and distinct.

With this apparatus I have transcribed many records of the principal vowels of our spoken English, but have as yet made a careful study only of the records of the vowel *a*, that is, the sound heard in such words as *father*, *palm*, *part*, etc. Plate I gives a photograph of some of the curves which I have obtained. They are all waves of the same sound at different pitches, as explained at the side. They were sung by four different voices, 1, 2 and 3 being baritones, and 4 being a boy's voice with soprano register. I have placed at the side the number of vibrations to the second as determined by the pitchpipe used in the present series of experiments. In photographing them they have been reduced nearly three diameters, so as not to occupy too much space. A few specimen waves of the full size as transcribed are shown in Plate II.

In transcribing the record from the wax cylinder to the bromide paper the cylinder was made to revolve once in about nine minutes, the bromide paper moving at the rate of 23½ inches (the circumference of the drum) in one minute. Now the circumference of the wax cylinder is about six inches, hence it is obvious that abscissas were magnified about 35 times ($9:6::1:\frac{2}{3}$; $\frac{2}{3}:23\frac{1}{2}::1:35\frac{1}{4}$). Again, since in making the original records the wax cylinder was made to revolve twice a second, it is obvious that a sound of one

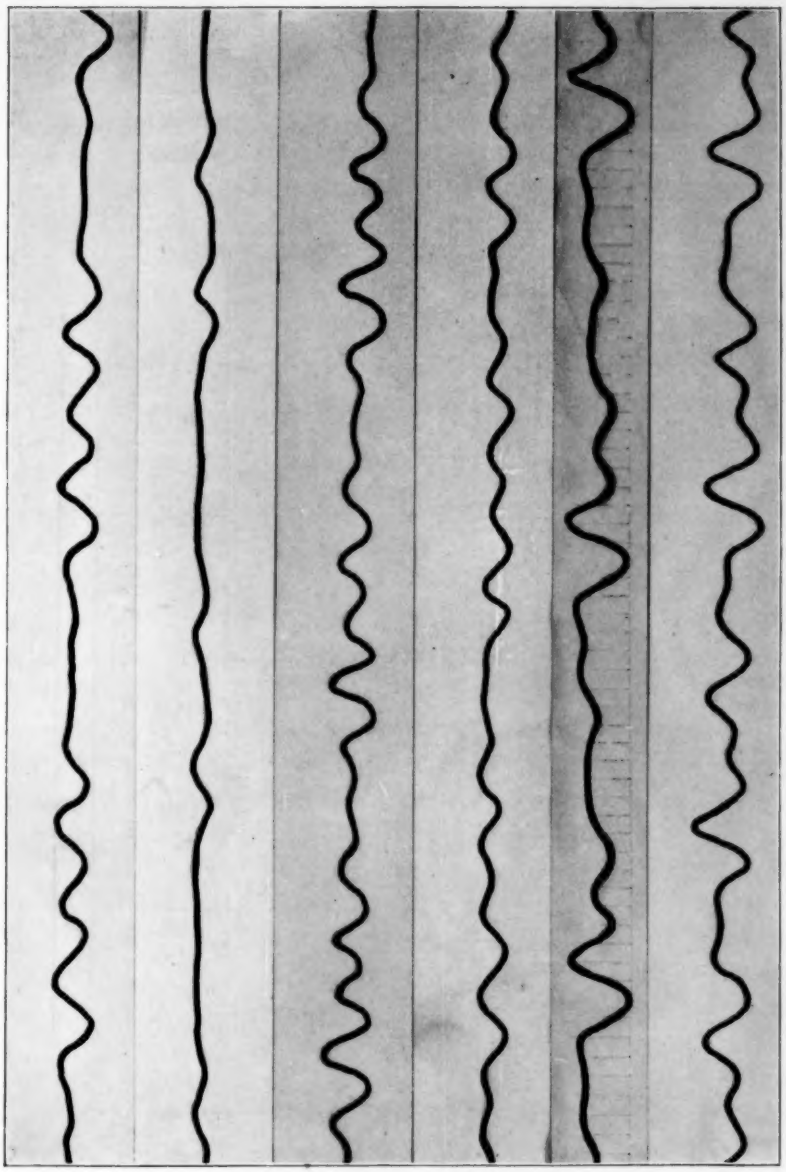
(To face page 196.)

CURVES OF THE VOWEL A.



BEVIER: ACOUSTIC ANALYSIS OF THE VOWELS.

(To face page 196.)



BEVIER: ACOUSTIC ANALYSIS OF THE VOWELS.

This plate reproduces in full size some of the curves shown in Plate I.

second's duration would trace a sinuous line on the bromide paper about 35 feet in length. For a tone at the pitch d (288), the wave-length is therefore about 1½ inches, and at D (144) about 3 inches. In the plate the lines represent therefore about $\frac{1}{56}$ part of a second. These ratios were found to be in practice convenient, but provided that the pitch is in each case carefully registered there is no particular importance in preserving precisely the same relations. The fundamental waves are perfectly distinguishable by the eye alone, and if the pitch is known all the rest is a mere matter of computation. The slow movement of the wax cylinder in transcription is however very important, because we avoid in this way any tremors in the arm which bears the mirror, which otherwise would falsify the record. In the present series of experiments I have employed a speed less than one thousandth of the original velocity, and for some vowels of high resonance pitch (especially i, as in *pique*) I should be inclined to reduce the speed still more. Though the necessity for such slow motion makes experimentation somewhat laborious, since it requires 17 minutes to transcribe a sound of one second's duration, still the necessary preliminaries are so much more exacting of time that an hour more or less in actual transcription does not make much difference.

In one further detail my experience may be of use to other investigators. A cylinder which it is proposed to use in such studies must be carefully planed beforehand. Inequalities which are of no consequence in its ordinary use show as mountainous irregularities when the ordinates are magnified one thousand times. After a cylinder has been planed so that inequalities of this sort are negligible, the desired record should be made and transcribed with as little delay as possible, for the wax is quite sensitive to changes of temperature, and after being left over night is noticeably less regular than when first planed. So, too, after planing it must not be removed from the mandrel and replaced before being used, for it is impossible to replace it so exactly in its former position, but that it will when replaced show again more or less eccentricity.

The waves obtained, specimens of which are shown in Plates I. and II., were subjected to the usual Fourier analysis. In the longest waves, or waves of lowest pitch, 36 ordinates were meas-

ured, and the overtones up to the 16th were computed. For the shortest 12 measurements, giving the first four overtones, were found to be sufficient. Intermediate waves were measured in 20 or 24 places, according to their pitch. In no case were any overtones higher than the 10th of large enough amplitude to merit consideration. The subjoined table gives some specimen analyses running from $A_1\#$ (with 113 vibrations to the second according to the pitch-pipe used) to d′ (with 576 vibrations to the second). They represent four different voices, and establish with my other material, I believe, a fairly accurate acoustic definition of *a*. For a fuller exposition of these results I refer to an article soon to appear in "Die Neueren Sprachen."

	I.	II	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
$A_1\#$	113	226	339	452	565	678	791	904	1017	1130	1243
2	9.9	15.4	2.5	.8	**11.5**	**16.1**	3.3	8.1	**21.2**	7.9	3.2
D	144	288	432	576	720	864	1008	1152	1296	1440	1584
2	32.9	4.3	1.9	8.5	**14.8**	2.1	8.8	**13.5**	7.2	1.3	4.7
F	171	342	513	684	855	1026	1197	1368	1539	1710	1881
3	5.6	4.8	2.9	**17.5**	5.0	**33.1**	**19.9**	2.1	6.1	1.9	1.1
A#	226	452	678	904	1130	1356	1582	1808	2034	2260	2486
1	9.2	3.6	**31.6**	8.0	**31.0**	2.6	6.2	1.4	.8	1.2	1.4
d	288	576	864	1152	1440	1728	2016	2304			
1	5.4	**18.2**	8.0	**57.3**	3.0	1.3	3.2	3.6			
f#	362	724	1086	1448	1810	2172	2534	2896			
4	9.5	**14.3**	**42.9**	**16.5**	9.5	2.5	3.5	1.3			
a	426	852	1278	1704	2130						
4	5.7	**16.5**	**61.9**	6.0	6.9						
d′	576	1152	1728	2304	2880						
4	21.4	**68.0**	4.0	5.6	1.0						

N B. In this table the fundamental is marked I, the first overtone II, the second III, etc., following the common, but somewhat misleading practice. I have not thought it worth while to adopt Ellis's "partial tone" instead of the familiar "overtone."

It will be sufficient here to describe briefly the conclusions to which I have arrived. The vowel *a* at any pitch, and pronounced by any voice, contains the following elements:

1st, The fundamental, with the first two or three overtones, *i. e.*, the octave above the fundamental, the fifth, and the second octave.

The fundamental varies greatly in relative amplitude for reasons which I do not as yet attempt to formulate. The overtones are generally very weak, unless reinforced by the mouth resonance as set forth below.

2d, and most characteristic for the identity of the vowel; the overtone or overtones whose frequencies of vibration chance to fall between 1000 and 1300 vibrations to the second, the maximum seeming to lie at about 1150. This is the main resonance of the mouth when formed to utter this vowel, and remains remarkably constant no matter what the fundamental pitch may be. If the fundamental has 144 vibrations to the second overtones VII., VIII. and IX., with frequencies of 1008, 1152, and 1296 respectively, will all be present, but VIII., with 1152 vibrations to the second, in much the largest amplitude. If the fundamental has 320 vibrations to the second overtones III. and IV. will be present, with 960 and 1280 vibrations to the second respectively, but IV. will be much the more prominent, III. being very weak since it falls below the region of strong resonance.

3d. The overtone or overtones whose frequencies of vibration chance to fall between 575 and 800 vibrations to the second for men's voices, with a maximum at about 675, or between 675 and 900 with a maximum at about 800, for the voices of women and children. This is presumably the resonance of mouth and throat cavities resounding as one vessel. It is not nearly as constant as the main resonance region explained above, and seems to vary between individuals and classes of voices far more than the other. It is however very important and at one pitch (A#, = 226) has an amplitude (not however an energy) a little greater even than the main resonance. If the fundamental has 144 vibrations to the second we shall find accordingly overtones IV. and V. present whose frequencies are 576 and 720 respectively, but V. being nearer the point of maximum resonance in this region will have the greater amplitude. At A# (=226) we shall find overtone III., with 678 vibrations to the second very prominent. My analyses reveal for the vowel *a* no other region of resonance except these two.

I subjoin a tentative chart (Fig. 2) representing the resonance curve for the *a*-position of the man's mouth. In this I have made the

frequency of vibration the abscissa and the amplitude of vibration the ordinate. Were this based on a long series of observations to eliminate individual and accidental elements we could thus plot a curve which could be taken as the standard resonance curve characteristic of the vowel. It would be practically an objective definition of the vowel, deviations from which in individual cases would be such as would not affect materially the character of the vowel.

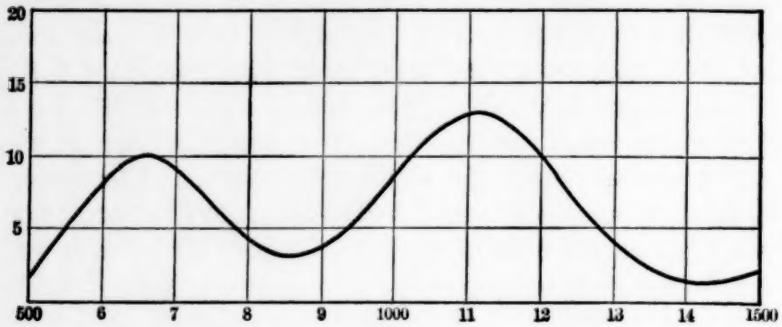


Fig. 2.

The above curve (Fig. 2) is drawn to represent simply amplitude percentages. The "energy" curve, in which ordinates are proportionate to the product of the squares of amplitudes and the squares of frequencies (E varries as a^2n^2) is perhaps even more significant. A tentative energy curve follows:

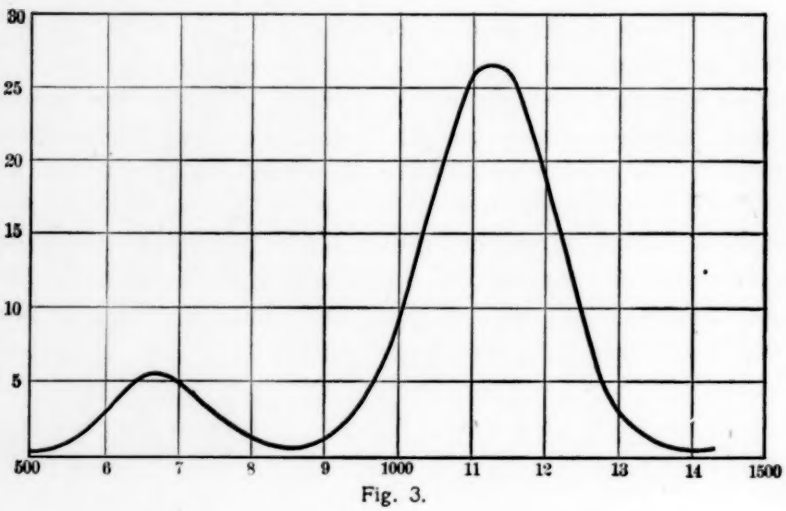


Fig. 3.

Many important questions arise which I do not as yet attempt to answer. A preliminary discussion of some of them will be found in the article to which I have already alluded. My main purpose here is to call attention to a means of experimentation which I am convinced will prove of great use in further researches.

A word as to the mathematical analysis by means of Fourier's theorem may be helpful. It is well to use the average ordinates obtained from a succession of adjacent waves. I say adjacent waves because no matter how steady the voice has been the waves are apt to change slightly in character as the sound proceeds, and though adjacent waves are often, so far as the eye can detect, perfectly similar, it is rarely possible to obtain a sequence of more than a dozen or so which are to the eye exactly alike. Changes of pitch, timbre or intensity so slight as to escape the notice of the ear cause very noticeable modifications in the wave-form, and make it illegitimate to average the measurements of any save adjacent waves. As the succession of waves is examined it will generally be seen that a change is in progress which, though slow,. results in the course of a small fraction of a second even in quite a marked difference. An analysis at two different points of the same utterance gives quite a different succession of measurements for ordinates, but the results of a mathematical computation are very similar. Before this matter can be really settled it will be necessary to analyze each wave of a series from beginning to end of an individual utterance. A sufficient number of such computations will probably throw light on this very interesting and difficult subject.

After the necessary measurements have been obtained the analysis is made by means of the familiar formulæ derived from Fourier's theorem, but the labor, particularly when it is necessary to use as many as 36 ordinates, is by no means small. I am indebted to my colleague, Robert W. Prentiss, M.S., Professor of Mathematics in Rutgers College, for a method of arranging the formulæ which has greatly abridged the labor. He is preparing an explanation of his arrangement which will be published shortly.

NOTE ON THE VARIATION OF THE SPECIFIC HEAT OF WATER BETWEEN 0° AND 100°C.

BY H. L. CALLENDAR AND H. T. BARNES.

THE present note which it is thought would be of interest to many of the readers of the PHYSICAL REVIEW is, with a few changes made to introduce later results, almost a reprint of the report communicated by the authors at the meeting of the British Association at Dover (Sept., 1899). In 1897, during the Toronto meeting, a preliminary note was communicated to the same society, in which the authors described briefly a new method for determining the specific heat of a liquid in terms of the international electrical units. At that time the method had only been roughly applied to the cases of water and mercury. The preliminary apparatus, however, was exhibited to several members of Section A on the occasion of their visit to McGill University. One of the main objects of the work was the determination of the variation of the specific heat of water over the range 0° to 100°C. for which the method is peculiarly suited. Shortly after the commencement of the work one of the authors (H. L. C.) was called to London to fill the Quain Chair of Physics in University College, leaving the work in the sole charge of H. T. B.

The general principle of the method, and the construction of the apparatus will be readily understood by reference to the diagram of the continuous-flow electric calorimeter given in Fig. 1. A steady current of water flowing through a fine tube, *AB*, is heated by a steady electric current in a central conductor of platinum. The steady difference of temperature between the inflowing and outflowing water is observed by means of a differential pair of platinum thermometers at either end. The bulbs of these thermometers are surrounded by thick copper tubes, which by their conductivity serve to equalize the temperature, and to prevent the generation of heat by the current in the neighborhood of the bulbs of the ther-

mometers. The leads *CC* serve for the introduction of the current, and the leads *PP*, which are carefully insulated, serve for the measurement of the difference of potential on the central conductor. The flow tube is constructed of glass, and is sealed at

Fig. 1.

either end, at some distance beyond the bulbs of the thermometers, into a glass vacuum jacket, the function of which is to diminish as much as possible the external heat loss. The whole is enclosed in an external copper jacket (not shown), containing water in rapid circulation at a constant temperature maintained by means of a very delicate electric regulator.

The general equation of the method may be stated in the following form:

$$JMd\theta + H = ECt.$$

The difference of potential E on the conductor is measured in terms of the Clark cell by means of a Thomson-Varley slide potentiometer, very accurately constructed and calibrated. The current C is also measured by observing the difference of potential on a standardized resistance R included in the circuit.

The Clark cells employed in this work were "crystal" cells [1] of the B. O. T. pattern and hermetically sealed cells. They were kept immersed in a regulated water bath at a constant temperature, near 15° C., and have maintained their relative differences constant to a few parts in 100,000 since they were made in 1895.

The resistance R consists of two one-ohm coils in parallel, each made of four bare platinum-silver wires in parallel wound on mica frames and immersed in paraffin oil at a constant temperature. The coils were annealed at a red heat after winding on the mica frames, and are not appreciably heated by the passage of the electric currents employed in the work. The two one ohms are repeatedly

[1] H. L. Callendar and H. T. Barnes, Proc. Roy. Soc., 62, 117 (1897).

standardized by comparison with an oil immersed certified one ohm manganin standard of the English Electrical Standards Committee, and have not changed their resistance since being made by as much as 5 parts in 100,000.

The time of flow t of the mass of water, M, was generally about fifteen minutes, and was recorded automatically on an electric chronograph reading to .01 second, on which the seconds were marked by a standardized clock.

The letter J stands for the number of joules in one calorie at a temperature which is the mean of the range $d\theta$, through which the water is heated.

The mass of water, M, was generally from 400 to 600 grammes. After passing through a cooler, it was collected and weighed in a tared flask in such a manner as to obviate all possible loss by evaporation.

The range of temperature was generally about 8° in the series of experiments on the variation of J, but other ranges from 1° to 12° were tried to test the theory of the method. The thermometers were read to the ten-thousandth part of a degree, and the difference was probably in all cases accurate to .001° C. This order of accuracy could not have been possible with mercury thermometers under the conditions of the experiments.

The external loss of heat, H, was very small, owing to the perfection and constancy of the vacuum attainable in the sealed glass jacket. It was determined and eliminated by adjusting the electric current so as to secure the same rise of temperature, $d\theta$, for widely different values of the water-flow.

The great value of the continuous-flow method as compared with the more common method in which a constant mass of water at a uniform temperature is heated in a calorimeter, the temperature of which is changing continuously, is that in this method there is practically no change of temperature in any part of the apparatus during the experiment. There is no correction required for the thermal capacity of the calorimeter; the external heat loss is more regular and certain, and there is no error due to the lag of the thermometers. Another distinct advantage is that the steadiness of the conditions permits the attainment of the highest degree of accuracy in the instrumental readings.

In work of this nature it is recognized as being of the utmost importance to be able to detect and eliminate constant errors by varying the conditions through as wide a range as possible. In addition to varying the electric current, the water-flow, and the range of temperature, it is possible with comparatively little trouble to alter the form and resistance of the central heating conductor, and to change the glass calorimeter for one with a different degree of vacuum, or a different bore for the flow tube. Several different calorimeters were thus employed, and the agreement of the results, on reduction, affords a very satisfactory test of the accuracy of the method.

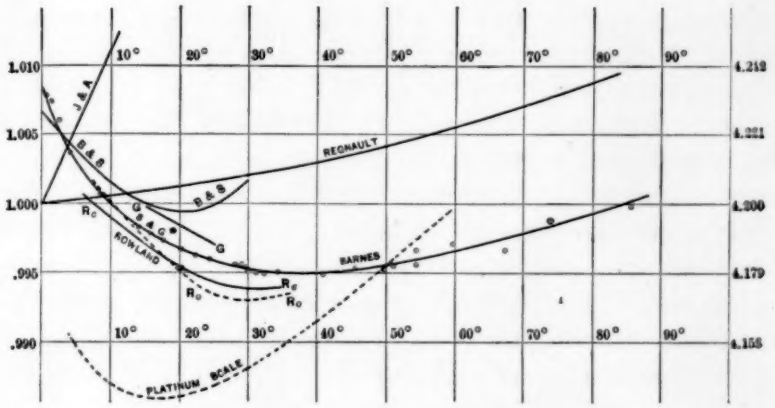


Fig. 2.

Variation of the Specific Heat of Water between 0° and 100° C.

J. & A. Jamin and Amaury, 1870.
B. & S. Bartoli and Stracciati, 1891.
R_o. Rowland's Original Values, 1880.
R_c. Rowland's Corrected Values, 1898.
G. Griffiths, 1893.
S. & G. Shuster and Gannon, 1893.
⊙ Authors' Values, 1899.
} Lord Rayleigh's Value for the Clark Cell, Assumed.
* Authors' at 20.°2 C.
} Kahle's and Carhart's Identical Clark Cell Values, Assumed.

The general results of the investigation, so far as it is possible to give them for publication at present, may be seen by reference to the plot given in Fig. 2, which includes also the results of other ob-

servers, to the same scale. The curve marked Regnault represents the well-known formula of Regnault which has been adopted as the basis of much calorimetric work. This formula was confessedly approximate, and was deduced from experiments on mixing water at high temperatures with water at 15° C. The method could not be expected to give any information with regard to the variation of the specific heat at ordinary temperatures. The experiments of Jamin and Amaury (J. and A.), by the method of electric heating, gave a very rapid increase of the specific heat at low temperatures, but the science of electrical measurement, and the difficulties of the electrical method, were not at that date sufficiently known to render the results of any value.

Rowland's original curve (R_o) is shown by the dotted line, and with it his corrected values[1] (R_c) are given by the smooth line. His original results, obtained by Joule's method, were expressed in terms of his own air thermometer, and showed, for the first time, how rapidly the specific heat of water diminishes as the temperature rises from 0° to 30° C. The corrected values are those obtained by reducing his thermometers to the Paris scale. The effect of this correction is to lower the temperature at which the specific heat is 4.200 joules from 10° to 7° C. and to diminish the temperature coefficient. In the plot in Fig. 2 the right hand margin gives the scale of joules in absolute measure.

The experiments of Bartoli and Stracciati (B. and S.) were made by the method of mixtures, and are expressed in terms of a thermal unit at 15° C. Their curve bears a general resemblance to that of Rowland, but shows a minimum point at 20° C. The errors and limitations of this method are well known, and it is difficult to suppose it capable of any high degree of accuracy, or to think otherwise than that the excessive lowering of the minimum point is due to some error not eradicated by mere repetition of similar experiments.

The experiments of Griffiths (G.) between 15° and 25° were made by observing the rate of rise of temperature of a mass of water heated by an electric current. His work threw a flood of light on the difficulties of electric calorimetry, and explained the failure of

[1] William S. Day, PHYSICAL REVIEW, 7, 193 (1898).

previous observers to obtain satisfactory results by this method. Over the range of his experiments he found approximately the same rate of diminution of the specific heat as that given by Rowland.

The curve marked by circled dots in the figure, extending from 0° to 86° C. represents the results so far obtained in the present investigation. The points represented are samples of single observations with different calorimeters, and give an idea of the order of accuracy attainable by this method. The accuracy of course diminishes as the temperature rises, owing to the greater difficulty of obtaining satisfactory regulation in the water-jacket at the higher points.

The curve shows clearly that the minimum point occurs at 40° instead of 30°. The experiments of Rowland did not extend sufficiently beyond his minimum point to obtain a satisfactory determination. The value of the specific heat could not be determined by his method with the same accuracy at the extremities of the range as in the middle, and all the probable errors of the method would be greatly increased as the temperature of the calorimeter was raised above its surroundings. In particular, the corrections and changes of zero of the mercury thermometers, and the rate of external heat loss, would be excessive at the higher points. In the present work, however, there are no thermometric difficulties of this nature, owing to the use of platinum thermometers, and the external heat loss increases very little as the temperature is raised, because the external water-jacket is always at the same temperature as the inflowing water, so that the mean excess of temperature is always nearly the same. Another indication that the temperature of minimum specific heat is not far below the middle of the range is given by the experiments of Regnault, and more recently by those of Reynolds and Moorby, on the mean specific of water between 0° and 100° C. Their results by entirely different methods agree in showing that the mean specific heat over the whole range does not greatly exceed the value at 20° C.

The present work shows that the specific heat of water approaches an exceedingly high value at 0°. The observations at 0.6°, 1.5°, 2° and 4° were obtained by using rises of temperature of

1°, 3°, 4° and 8° with the inflow water nearly at 0°. This rapid increase, shown by these points, was foreseen by Rowland, but not shown in his work.

It is interesting to compare the absolute values of the specific heat deduced by the electrical method with those of Rowland by the mechanical method. For this purpose the authors' results, and those of Griffiths (G.), and of Shuster and Gannon (S. and G.), have been reduced to joules on the assumption that the absolute value of the E. M. F. of the Clark cell is that found by Glazebrook and Skinner, assuming Lord Rayleigh's value of the electro-chemical equivalent of silver, and taking the international ohm as correct. It has been pointed out that the results of Griffiths would be brought into harmony with those of Rowland by supposing that the true E. M. F. of the Clark cells employed was about 2 millivolts lower, or one part in 700. The authors' results, however, lie about midway between those of Rowland and Griffiths, and would require a correction of only 1 millivolt, if the whole of the difference were to be ascribed to the Clark cell. It is not at all likely that the cells used in this work can have exceeded the B. O. T. standard by so much as 1 millivolt, or that the resistance standards can have been incorrect by as much as one part in 700. It is most likely that both the Clark cells and the resistance standards agreed with those used by Griffiths to within one or two parts in 10,000 and that the difference of the results is mainly to be attributed to the radical difference in the methods of calorimetry. In view of the recent determinations of the absolute value of the Clark cell made by Kahle and later by Carhart and Guthe, the authors' value at 20° C. is reduced assuming the new value of the Clark cell, *i. e.*, 1.4330 volts. This has the effect of lowering the specific heat and causing it to almost exactly coincide with Rowland's corrected value at the same temperature. The complete variation curve would then be lowered the same amount had the new Clark cell value been used in its deduction.

These and similar questions relating to the absolute values of the standards used do not affect the accuracy of the relative results as regards the variation of the specific heat of water with temperature. The relative results are regarded by the authors as being as accu-

rate as the present apparatus is capable of affording. By far the most important consideration affecting the form of the curve is the particular thermometric scale to which the results are reduced. If, for instance, the results were expressed in terms of the platinum scale, which differs from the absolute scale by only 0.38° C. at 50° C., when the divergence is a maximum, the curve would be that represented by the dotted line in the figure. The authors' variation curve is deduced from this by the usual parabolic formula, which gives results in practical agreement with the Paris scale.

Since the discussion of the thermal unit introduced by Griffiths at the British Association meeting of 1895, and partly in consequence of the general interest excited by that discussion, so many new facts have been brought out, and so much experience has been gained of the practical effect of the proposals then made, that it appears desirable to discuss more fully the bearing of the present work on the general question of the relation between the various thermal units.

Dieterici[1] made a determination of the mean specific heat in terms of the electrical units by means of a Bunsen ice-calorimeter. His result gives 4.233 joules as the value of the mean specific heat of water in absolute measure between 0° and 100° C.

Winkelmann[2] endeavored to connect this result with Rowland's at low temperatures by assuming a parabolic formula for the mode of variation, and taking the minimum value at 30.6° C. to be 0.9898 of the value at 0° C. This formula makes the ratio of the mean specific heat between 0° and 100° C. to the specific heat at 20° C. to be 1.0120. According to Regnault's formula the same ratio would be 1.0038. If we take Rowland's corrected value at 20° C. as 4.181 joules, the mean value between 0° and 100° would be 4.197 joules according to Regnault, but 4.233 joules according to Winkelmann. The latter gives a remarkable coincidence with Dieterici, in consequence of which the formula of Winkelmann has been frequently quoted and employed in physical investigation. It must be remarked, however, that Rowland's curve is not even approximately parabolic and that the range covered by his observations is hardly

[1] Wied. Ann., 33, 417 (1888).

[2] Handbook of Physics, Vol. II., Pt. 2, p. 338.

sufficient to justify this method of treatment. It must also be observed that the values given by Winkelmann's formula for the specific heat in the neighborhood of 100°, and still more at higher temperatures, are so large that they cannot possibly be reconciled with the experiments of Regnault and other good observers.

Griffiths[1] came to the conclusion from a comparison of his experiments on the latent heat of evaporation of water at 30° C. and 40° C. with those of Dieterici at 0° C. expressed in terms of the mean specific heat, and with those of Regnault on the total heat or steam at 100° C. that the mean specific heat must be very nearly identical with the specific heat at 15° C., although Regnault's direct experiments made the ratio from 0.5 per cent. to 1 per cent. larger. At his suggestion Prof. Joly performed the inverse experiment of determining the mean specific heat between 12° and 100° with his steam calorimeter in terms of the latent heat of steam at 100° taken as 536.63 times the thermal unit at 15° C. The result of this experiment was to make the mean specific heat appear nearly 0.5 per cent. smaller than the specific heat at 15° C. If we suppose that the inversion of the experiment would tend to reverse the error of the original determination of the latent heat, the result would appear to be strongly in support of Griffith's contention.

Peabody, in the preface of his "Tables of the Properties of Saturated Steam" (1896), as a result of a careful discussion of Rowland's and Regnault's experiments, adopts Rowland's values from 0° to 40°, and expresses his results in terms of the mean specific heat between 15° and 20°. He finds that Regnault's experiments may be sufficiently represented in terms of this unit by assuming the specific heat to be constant and equal to 1.008 between the limits 45° and 155°, and constant and equal to 1.046 between the limits 155° and 200° C. This assumption would make the mean specific heat between 0° and 100° have the value 1.0044 in terms of the specific heat at 17.5° C., or the value 1.0056 in terms of the specific heat at 20° C., assuming Rowland's coefficient of diminution. The general effect of these changes is to make the tables agree fairly well throughout with Regnault's experiments, but the method can only be justified on the ground of expediency, and can hardly be

[1] Phil. Trans., 7, 318 (1895).

regarded as a satisfactory reconciliation of conflicting evidence on account of the assumed discontinuities in the specific heat.

Shaw[1] gives a similar reduction of Regnault's experiments by means of Rowland's original table, but tabulates only the total heat in joules at each point between 100° and 180° C. His reduction shows a similar flattening of the curve between 100° and 150°, as compared with Regnault's formula. This may be a physical fact, but might also be explained by supposing that the earlier experiments at 108° to 120° were about 0.4 per cent. too high. Shaw's reduction expressed in terms of a thermal unit at 20° C. is given for comparison in the table.

Recently a direct determination of the mean specific heat in terms of the mechanical units has been made by Reynolds and Moorby on a large scale with Reynolds' break and a steam engine. Their results expressed in absolute measure is 4.1832 joules, and is entitled to very great weight on account of the minute accuracy of the measurements, and the full discussion of possible sources of error. It exceeds the value found by Rowland at 20°C. by only one part in two thousand, but is no less than 1.20 per cent. smaller than the mean value found by Dieterici. This is a discrepancy far too large to be explained by any uncertainty in the values of the electrical units.

Accepting the trustworthy measurements of Reynolds and Moorby it is clear that the minima of specific heat at 20° and 30° indicated by the work of Bartoli and Stracciati and of Rowland respectively, must be due to some source of error in their methods, and that all formulæ hitherto proposed for the mode of variation of the specific heat between 0° and 100° must be abandoned.

It is possible, however, to deduce a more satisfactory comparison of the results of Rowland with those of Reynolds and Moorby by means of the present series of experiments, on account of their great range, and the close agreement of the individual observations. Neglecting for the present the rapid change of the specific heat in the immediate neighborhood of 0° C., it may be observed that all the authors' observations between 10° and 60° (with the exception of one at 55°) are represented to about one part in 5,000 (*i. e.*,

[1] B. A. Report, 1896, p. 162.

within the limits of agreement of the observations with different calorimeters at any one point) in terms of the minimum value S_{40} at 40° C., by the simple formula

$$S_t = S_{40}(1 + .0000045(t - 40°)^2).$$

which gives for the mean specific heat between 0° and $t°$ the formula

$$S_0^t = S_{40}(1.0072 - .00018t + .0000015t^2).$$

If this formula could be assumed to hold beyond these limits over the whole range 0° to 100, the ratio of the mean specific heat between 0° and 100° to the specific heat at 20° would be 1.0024. Assuming Rowland's 4.181 joules at 20°, this ratio would give the value 4.191 joules for the mean specific heat, a result obviously in excess of Reynolds' and Moorby's 4.183 joules.

It is evident from the observations at higher temperatures that the variation curve is not symmetrical, but flatter between 60° and 100°. The rate of change of the specific heat at 100° as given by the above formula, if extrapolated, is more than twice as great as that given by Regnault, and at 200° about four times as great. The experiments of Regnault apply particularly to this portion of the range, for which they have remained the standard, and have been so universally adopted. It would be desirable to retain his formula for the present, with such change as would make it fit the present experiments. It will be readily seen by reference to the figure that Regnault's curve is very nearly parallel to the authors' curve between 40° C. and 86° C. The two curves can then be very accurately fitted over this range by simply subtracting a constant quantity from the values given by Regnault's formula. This method leads to results, which require the simplest modification of existing tables.

Adopting the authors' formula between 10° and 60°, and the corrected formula of Regnault from 60° to 100°, the ratio of the mean specific heat between 0° and 100° to the specific heat at 20° is 1.0014. Taking Rowland's value as 4.181 joules at 20°, this ratio would give 4.1868 for the mean specific heat, which exceeds the value found by Reynolds and Moorby by less than one part in a thousand—a discrepancy so small as to be within the limits of

TABLE OF THE SPECIFIC HEAT OF WATER.

RANGE 0° TO 60°C.

FORMULA.

$$S_t = 0.9982 + 0.0000045\,(t - 40°)^2.$$

t°C.	Joules.	S_t	$S_{40}{}^t$	h Authors' Formula.	Rowland (reduced).	
0	4.203	1.0054	—	—	—	
5	4.196	1.0037	1.0045	5.023	5.023	
10	4.190	1.0022	1.0037	10.037	10.044	
15	4.185	1.0010	1.0030	15.045	15.054	
20	4.181	1.0000	1.0024	20.048	20.057	
25	4.178	0.9992	1.0018	25.045	25.053	
30	4.176	0.9987	1.0013	30.039	30.043	
35	4.174	0.9983	1.0009	35.032	35.039	
40	4.174	0.9982	1.0006	40.024	Peabody	
45	4.174	0.9983	1.0003	45.016	45.000	
50	4.176	0.9987	1.0001	50.008	50.040	
55	4.178	0.9992	1.0000	55.002	55.080	
60	4.181	1.0000	1.0000	60.000	60.120	

Range 60° to 220°C. Regnault (Corrected).

Formula $S_t = 0.9944 + 0.00004t + 0.0000009t^2$.

60	4.181	1.0000	1.0000	60.000	60.12	
65	4.184	1.0008	1.0000	65.002	65.16	
70	4.188	1.0016	1.0001	70.008	70.20	
75	4.191	1.0024	1.0002	75.018	75.24	
80	4.195	1.0033	1.0004	80.032	80.28	
85	4.199	1.0043	1.0006	85.051	85.32	
90	4.203	1.0053	1.0008	90.075	90.36	
95	4.207	1.0063	1.0011	95.105	95.40	
100	4.212	1.0074	1.0014	100.138	100.44	
110	4.222	1.0097	1.0020	110.22	110.67	Shaw.
120	4.232	1.0121	1.0028	120.33	120.73	
130	4.243	1.0148	1.0036	130.47	130.80	
140	4.255	1.0176	1.0045	140.63	140.88	
150	4.267	1.0206	1.0055	150.82	151.01	
160	4.281	1.0238	1.0066	161.05	161.20	
170	4.295	1.0272	1.0077	171.31	171.61	
180	4.310	1.0308	1.0089	181.60	182.14	
190	4.326	1.0345	1.0102	191.94	—	
200	4.342	1.0384	1.0115	202.31	—	
210	4.359	1.0425	1.0130	212.72	—	
220	4.377	1.0467	1.0145	223.18	—	

possible error even in the case of these two extremely accurate determinations.

The annexed table has been constructed on the basis of the above considerations and represents, by the authors' formula combined with the corrected formula of Regnault, the variation of the specific heat of water between 0° and 220° C. The absolute measure at 20° C. given by Rowland, *i. e.*, 4.181 joules, is taken as the basis of column 2. The values of the specific heat are worked out assuming a unit at 20° C. and neglecting the rapid increase below 10° C. The general effect of this table is to diminish the extent of the variation hitherto assumed, but it is believed that the results here tabulated are within the limits of error of all the best determinations. The order of agreement may be inferred from a comparison of the values of h, the total heat of the liquid, given in the last two columns. The agreement with Rowland is within 1 in 3,000, between 10° and 40°, and with Regnault within 1 in 1,000 at 160° C. The variations of Regnault's individual observations exceed 5 parts in 1,000.

The values of the total heat h are obtained by integrating the specific heat from 0° to t° by the formula. By adding below 10° the constant quantity .020 to the value of h as given in the table, account is taken of the rapid increase at the freezing point.

In conclusion it may be stated that the work is being rapidly continued to verify the points obtained above 60° C. The observations at the higher points are exceedingly difficult and tedious to obtain but with the present arrangements designed especially with this object in view observations as high as 95° C., will probably be obtained.

MACDONALD PHYSICAL LABORATORY, MCGILL UNIVERSITY, Feb. 3, 1900.

THE MAGNETIC MOLECULAR SUSCEPTIBILITY OF SALTS OF THE IRON GROUP.

By O. Liebknecht and A. P. Wills.[1]

GUSTAV WIEDEMANN was the first to undertake magneto-chemical investigations in regard to the behavior of the paramagnetic salts of the metals: chromium, manganese, iron, cobalt, nickel and copper. He used a torsion method with a non-uniform field.[2] He found that the quantity defined by him as the "Molecularmagnetismus" is nearly independent of the solvent, the concentration, and especially of the nature of the anions for a given temperature and cation of a given valency. The differences always exceeded the experimental errors and amount in general to 2 or 3 per cent. Therefore he found a mean value for a given cation and called it the "Atommagnetismus." The atomic magnetisms of the manganous, ferrous, cobaltus and nickelous salts were as $a + 2b$, $a + \frac{3}{2}b$, $a + b$, a, where $b = 1.15a$; that of the ferric salts exceeds that for the ferrous salts by about 15 per cent.

Not long since G. Jäger and St. Meyer[3] published some striking measurements made with a modification of the Quincke manometric method. They drew the conclusion that the atomic magnetisms of manganese, iron, cobalt, nickel are as $6:5:4:2$; this agrees with the proportion given above if $a = b$. Their results were obtained from the chlorides, sulphates and nitrates; with manganese, cobalt and nickel, only the bivalent salts could be used; on the other hand the value for iron was taken as the mean of the results for ferric chloride, ferrous sulphate and ferric nitrate.

[1] The chief results were communicated to the Physikalische Gesellschaft on the 30th of June, 1899; many results were still outstanding.

[2] G. Wiedemann, Pogg. Ann., 126, p. 1, 1865; 135, p. 177, 1868; Wied. Ann., 5, p. 45, 1878; P. Plessner, Wied. Ann., 39, p. 336, 1890; G. Quincke, Wied. Ann., 24, p. 392, 1885. G. Wiedemann, Lehre von der Elektricität, 2. Aufl. 3, §§ 1266–1291, 1895. J. Koenigsberger, Wied. Ann., 66, p. 698, 1898.

[3] G. Jäger und St. Meyer, Wien. Ber. (2), 106, pp. 594, 623, 1897; 107, p. 5, 1898.

In later articles Jäger and St. Meyer use for ferrous chloride the relative number 3 instead of 5 as above; further, they obtain from chromic chloride and chromic sulphate the number 2.5 for chromium.

In the light of these results it seemed to us desirable to make new determinations using a different method. We have made quantitative determinations upon 36 salts of the five metals of the iron group and of copper. Great stress was laid upon the procuring of the purest material possible, and all salts in which there was danger of rapid decomposition were discarded. In general, we have studied the sufficiently soluble fluorides, chlorides, bromides, iodides, sulphates and nitrates; for the reason just mentioned, it was not possible to study many of the iron and chromium compounds. The accuracy of our final results may vary between 2 and 5 parts in 1,000, according to the method used in the chemical analysis.

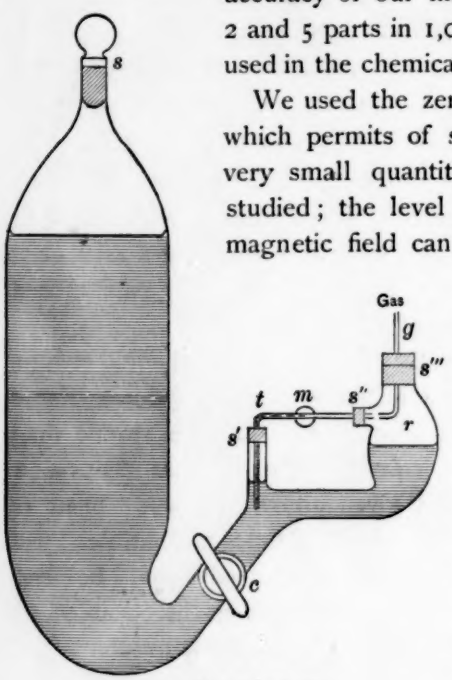


Fig. 1. ¼ natural size.

We used the zero method of Prof. du Bois,[1] which permits of successful manipulation with very small quantities of the substances to be studied; the level of the capillary tube in the magnetic field can be so adjusted that the unmagnetic solution can be prepared with great precision so as to be well within the limits of error in the subsequent chemical analysis. Briefly, the procedure is as follows: A conveniently strong paramagnetic solution is prepared and then diluted with the diamagnetic solvent until the solution is unmagnetic. The practicability of the method is only limited by the susceptibility and solubility of the salt. Sometimes the method is inadmissible on this account as, for example, in the case of potassium chromate and bichromate and of

[1] H. du Bois, Wied. Ann., 35, p. 154, 1888; 65, p. 38, 1898.

potassium and calcium permanganate. These peculiarly constituted salts are well known to be but weakly paramagnetic; the similarly constituted dry K_2FeO_4 proved to be much more paramagnetic; the alkali solution decomposed so quickly that we were prevented from making a quantitative determination.

As a criterion for the unmagnetic condition of the solution, the behavior of its meniscus in a Quet's [1] capillary tube *t* in a magnetic field was observed (Fig. 1). The large mixing vessel had a capacity of about 600 ccm.; it could be closed by means of a glass stopper *s*, and could be separated from the rest of the apparatus by means of the glass stopcock *c*; the arm connected with the mixing vessel was so formed that fresh capillary tubes could be suitably introduced and fixed by means of the rubber stoppers at *s'* and *s''*. The space beyond the meniscus in the capillary tube and the space *r* could be filled with washed moist illuminating gas.[2] This apparatus was fixed to a suitable stand permitting a rotation about a horizontal axis perpendicular to the plane of the figure. The inclination of the capillary tube could be thereby regulated by means of a suitable adjusting screw; and, moreover, by means of a vigorous rotation of the apparatus about this axis a thorough mixing of the solution could be attained. At *m* is represented the end view of the truncated conical pole piece of the ring electro-magnet.

With a little practice a very short time sufficed to prepare an unmagnetic solution with an accuracy of one part in 1,000, so that upon excitation of the electro-magnet no noticeable motion of the meniscus took place. At each dilution the mixing apparatus was, of course, well shaken and each part well washed with the diluted solution, so that the solution should have in all parts the same concentration as at the meniscus. Any possible local change in the concentration due to magnetic influences would scarcely have time to be effected; furthermore, though such an effect theoretically

[1] Quet, Comp. Rend., 38, p. 562, 1854; E. Verdet, Oeuvres, 1, p. 199

[2] The susceptibility of illuminating gas was neglected; as far as known it amounts at a pressure of one atmosphere to less than one thousandth of that of water; compare M. Faraday, Exp. Res., 3, p. 502, 1855; G. Quincke, Wied. Ann., 34, p. 445, 1888; A. Toepler u. R. Hennig, Wied. Ann., 34, p. 796, 1888. An absolutely unmagnetic gas can be made after the manner of an unmagnetic solution by mixing a little oxygen with a diamagnetic gas; compare du Bois, l. c., p. 167; of course it is here tacitly supposed that the permeability of a vacuum serves as the unit in the usual conventional way.

exists, it has not been unmistakably shown experimentally.[1] In case the capillary is inclined toward the horizontal by a fraction of a degree, it is possible with a field of 40,000 c. g. s. units, to detect a differential susceptibility which does not exceed a hundred thousandth of that of water. On account of the above mentioned limits of error in the chemical analysis, it was useless to try for such accuracy as this, so that as a rule a much less sensitive adjustment was employed.

The procuring and cleaning of the capillary tubes offered at first some difficulties. Finally the freshest possible tubes from Thüringer glass were used, these being kept under water until required.[2] With these the mobility of the meniscus was satisfactory. Any influence of the breadth of the capillary tube used upon the concentration of the unmagnetic solution contained therein, could not be detected. This furnished, as is easy to see, an indirect proof that the capillary constants of unmagnetic solutions are quite unaltered in the magnetic field.

This independence of the surface tension of magnetic influences seems to obtain in general.

Brunner and Mousson[3] have fruitlessly sought such an action, whereby they seem to have overlooked the well known-Quincke effect of elevation (or depression) in the magnetic field, which, however, W. Wertheim[4] probably observed. Quincke[5] first undertook drop experiments with strong paramagnetic manganese and iron solutions; he found that the weight of a drop was unaltered by a uniform magnetic field and assumed, therefore, the constancy of the surface tension of such solutions. On the other hand, in a non-uniform field between conical pole pieces the drops of manganese chloride as of iron chloride were larger or smaller upon the excitation of the magnetism according as they formed under or above the shortest lines of force.

[1] Compare with G. Wiedemann, Electricität, 2, Aufl. 3, § 1205, 1895.

[2] Compare P. Volkmann, Wied. Ann., 66, p. 194, 1898.

[3] C. Brunner u. A. Mousson, Pogg. Ann., 79, p. 141, 1850.

[4] W. Wertheim, Comp. rend., 44, p. 1022, 1857; Pogg. Ann., 102, p. 595, 1857.

[5] G. Quincke, Pogg. Ann., 160, p. 586, 1877; Wied. Ann., 24, p. 375, 1885. Compare also Durchflussbeobachtungen by H. Dufour, Lum. Electr., 23, p. 337, 1887; likewise G. Jäger u. St. Meyer, Wied. Ann., 67, p. 711, 1889.

For a further investigation of these phenomena we constructed an apparatus (Fig. 2) by means of which the formation of the drop could take place at the nozzle *n* which was of about 1 mm. inside breadth, and at the proper pressure and at different rates, and moreover either in a uniform field of about 18,000 c. g. s. units between surface pole pieces, or in a non-uniform field of about 40,000 c. g. s. units between conical pole pieces *M* and *M'* and while the nozzle was placed in the position of greatest field intensity. The vessel *A* was in connection through *S* with the reservoir *B* in which the level of the liquid could be regulated. The space *r*, *r* could be connected through the cock *c* with a pump; the pressure regulated in this manner was read off on the manometer *m*. A number of experiments were carried out with this apparatus and, briefly stated, the results are as follows:

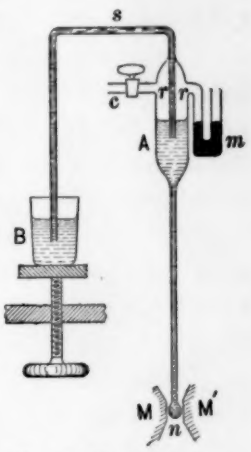


Fig 2. ⅙ natural size.

Paramagnetic solutions show in a uniform field, an increased rate of dropping when the magnetic force upon the liquid column acts downwards; through diminution of the pressure the original rate being again approximately established,[1] the weight of the drop suffers no change. On the other hand, we observe an enlargement of the drop in a non-uniform field; the form of the drop is then changed and depends upon the particular distribution of the field as regards the sense and manner in which it happens. These experiments confirm Quincke's results and conclusions.

Diamagnetic water shows in a uniform field a slower rate of dropping when the magnetic force is directed upwards and, therefore, against the hydrostatic pressure; under proper conditions the dropping may be quite stopped through excitation of the field. If the original rate of dropping be restored through increase of the pressure the weight of the drop suffers no change. In a non-uniform field the weight appeared less with the arrangement used, and more so the less uniform the field.

[1] This must be done because, as well known, the rate under ordinary conditions exerts a small secondary influence upon the weight of the drop.

Unmagnetic solutions are not at all influenced, as regards the magnitude of the drop, through excitation of the field if the drops fall in an atmosphere of illuminating gas. Toward air they behave, naturally, like a weakly diamagnetic liquid. This simple criterion has an application in the preparation of unmagnetic solutions; in accuracy this procedure is inferior to the method already described and the one, as a rule, used by us.

THEORY OF THE METHOD.

The extension of our knowledge of magnetic phenomena might be expected, from the first, in a thorough investigation of the thermo-magnetic and magneto-chemical processes. It would seem then to be not superfluous to give in this place, concisely as possible, the elementary conceptions connected with calculations on this subject. The reference of the magnetic moment to the unit of mass, once much employed, has been quite displaced in consequence of the advanced development of the mathematical theory of electromagnetism, because in mathematical physics the reference to the unit of volume is simpler. Professor du Bois [1] has shown that in some cases it is desirable to return to the original method, because the results are in many respects more easily comparable when the variable density is eliminated. Since magnetic processes are essentially molecular it is still better to refer them for stoichiometrical purposes to molecular masses.

In what follows m means molecular weight; M, mass; $\mathfrak{M}$, magnetic moment; $\mathfrak{S}$, specific magnetization, *i. e.*, moment per unit of mass; $\mathfrak{H}$, field intensity; i, specific susceptibility defined by the relation $i = \frac{\mathfrak{S}}{\mathfrak{H}}$.[2] The molecular susceptibility i_m is now defined by the equation

$$i_m = mi = \frac{m\mathfrak{S}}{\mathfrak{H}}.$$

In what follows, the subscripts l, w, s refer respectively to the solution, solvent and salt. On account of the additive properties,

[1] H du Bois, Phil. Mag. (5), 29, p. 293, 1890.

[2] If we designate, as customary, the density with D, the magnetization with $\mathfrak{J}$, the susceptibility according to the ordinary definition with κ, then is $\mathfrak{S} = \frac{\mathfrak{J}}{D}$ and $i = \frac{\kappa}{D}$. Compare J. Koenigsberger, Wied. Ann., 66, p. 698, 1888.

first shown by G. Wiedermann, of the quantities here coming into consideration, the following equation obtains for a solution in a uniform field

$$\mathfrak{M}_l = \mathfrak{M}_w + \mathfrak{M}_s.$$

The influence of form as well as the therewith connected magnetic interaction of the separate similar or dissimilar volume elements may be with the strongest paramagnetic solutions disregarded since the square of the susceptibility in comparison with unity is quite negligible. In particular for an unmagnetic solution $\mathfrak{M}_l = 0$ therefore $\mathfrak{M}_s = -\mathfrak{M}_w$, or $\mathfrak{S}_s M_s = -\mathfrak{S}_w M_w$. After division by $\mathfrak{H}$ we get

$$(1) \qquad \frac{i_s}{i_w} = -\frac{M_w}{M_s}$$

and the relative molecular susceptibility $\frac{i_m}{i_w}$ of the salt becomes finally

$$(2) \qquad \frac{i_m}{i_w} = -m\frac{M_w}{M_s},$$

i. e., equal to the negative product of the molecular weight into the mass ratio of the solvent and salt. This value of i_m holds not only for the particular concentration of the unmagnetic solution but quite generally;[1] whether, considering the accuracy of our new method, it is quite independent of the kind of solvent can only be decided by a special series of experiments; it changes markedly with the temperature.

Professor du Bois has shown that the behavior of an unmagnetic solution in fields of different intensities permits a conclusion as to the constancy of the susceptibility and has shown this constancy to exist with fields up to 10,000 c. g. s. units.

If the constitution of the unmagnetic solution measured by $\frac{M_w}{M_s}$, is independent of the field intensity, then it follows directly from equation (1) that the relative susceptibility with reference to water $\frac{i_s}{i_w}$ is also independent of the field.

[1] According to the results of various investigators; compare with J. Koenigsberger, l. c., p. 708.

[2] H. du Bois, Wied. Ann., 35, p. 155, 1888.

In fact, such a dependency was not found for any of the unmagnetic solutions investigated, and this holds for the extended range of fields between 2,000 and 40,000 c. g. s. units. Now it can be asserted with a probability bordering upon certainty that the variations of the susceptibility of water would not be followed exactly proportionately by those of the different salts. Therefore, the constancy of the absolute susceptibility of the dissolved salt, as of water, within the specified range of fields, follows from the constancy of the susceptibility of the dissolved salt relative to water.

Furthermore, it is very improbable that the susceptibility for weaker fields would be variable.[1] In the results to follow the constant susceptibility of water enters everywhere as a principal factor. We have the following determinations for this factor which have been recalculated so as to refer to a temperature of 18°, and to a vacuum; the susceptibility of air at one atmosphere pressure and 18° was taken as 0.023×10^{-6}.[2]

TABLE I.

	Temperature 18°.	Toward Vacuum.
1885	G. Quincke (most accurate v alue)	$\kappa = -0.797 \times 10^{-6}$
1888	H. du Bois	-0.831 "
1892	S. Henrichsen	-0.727 "
1895	P. Curie (mean value)	-0.788 "
1896	J. S. Townsend	-0.735 "
1898	J. Koenigsberger	-0.785 "
1899	G. Jäger–St. Meyer (mean value)	-0.645 "
	Mean value	$\kappa = -0.758 \times 10^{-6}$
Since $D_{18°} = 0.9987$, i_w becomes -0.759×10^{-6}		

In consideration of the obvious uncertainty of the value of the fundamental constant i_w and its temperature coefficient we have for the present designated it by x and taken the molecular

[1] Compare Vgl. F. Auerbach in Winkelmann's Handbuch der Physik, 3, 2 Abth., p. 217. Breslau, 1895.

[2] G. Quincke, Wied. Ann., 24, p. 404, 1885; H. du Bois, Wied. Ann., 35, p. 167, 1888; S. Henrichsen, Wied. Ann., 45, p. 53, 1892; P. Curie, Thése Nr. 840, p. 31, Paris, 1895; J. S. Townsend, Proc. Roy. Soc., 60, p. 186, 1896; Beibl. 20, p. 796, 1896; J. Koenigsberger, Wied. Ann., 66, p. 703, 1898; G. Jäger und St. Meyer, Wied. Ann., 67, pp. 427 u. 707, 1899. The old determinations of M. Faraday, E. Becquerel, J. Schuhmeister and the value of Théodore Wahner's which falls so far out are not considered.

susceptibility relative to it; and then in order to obtain approximate absolute values we have taken provisionally $x = -0.75 \cdot 10^{-6}$. A thorough discussion of the above values and further accurate new determinations would be desirable. So soon as these can be carried through with the accuracy with which the relative values $\frac{i_m}{x}$ are determined, the reduction of the latter to absolute numbers may be easily accomplished.

The constitution of an unmagnetic solution is variable with the temperature; we have therefore carefully maintained a normal room temperature of 18°C.[1] The unmagnetic solutions prepared according to this are then at higher (lower) temperatures somewhat diamagnetic (paramagnetic) because the temperature coefficient for the salt is always greater than for the water.

In case the latter were accurately known, the former for different salts could easily be determined.[2]

The Chemistry Details.

Most of the salts were pure preparations from Kahlbaum or Merck, and were, when possible, many times recrystallized before use. Most of the fluorides, bromides and iodides were prepared by one of us from pure carbonates. The nickel salts were procured from Kahlbaum as "cobalt-free" and the cobalt salts as "nickel-free"; the influence of the chemically unrecognizable impurities present cannot make a difference in the molecular susceptibility fonnd of more than 0.5-per-cent. solutions, which especially incline to decomposition, *e. g.*, MnF, MnCl, FeSo, FeCl, FeBr, were usually treated with a free acid; this was without noticeable influence on the results since the susceptibility of the acid added differs little from that of water; the ferrous iodide contained some free iodine. Where a gradual decomposition was to be feared, the solution was analyzed as soon as prepared; quickly decomposable solutions were not investigated, as already remarked; of course,

[1] Compare F. Kohlrausch und L. Holborn, Leitvermögen der Elektrolyte, Leipzig, 1898.

[2] In such measurements, an unmagnetic atmosphere should bound the liquid. The marked dependence of the susceptibility of oxygen relative to air upon the temperature, which has already been mentioned, would otherwise bring in a considerable error.

care was taken that no dilution or concentration change should take place after the solution was once prepared. The gravimetric analysis was carried out for the chromium salts by precipitating them with ammonia as hydroxides. The manganese solutions were precipitated with phosphorus-free hydrogen peroxide and ammonia as oxides and weighed as mangano-manganic oxides. The iron salts were determined in part with potassium permanganate by titration and in part precipitated with ammonia as hydroxides. Finally, the cobalt, nickel and copper were electrolytically precipitated, the two first in a neutral solution with ammonium oxalate and the copper in a solution of sulphuric acid containing a little nitric acid.

RESULTS.

Our quantitative results are collected into Table II. q designates the valency of the cation of the salt; a the atomic weight; the metals are arranged according to their increasing atomic weights.[1] The position of cobalt and nickel in the series is reversed, however, after mature consideration. For, according to the collective properties in the metallic or amalgamated condition, and in the condition as a paramagnetic compound, cobalt stands nearer to iron than does nickel; likewise for the chemical properties. In the column before the last is given the relative molecular susceptibility x, which is calculated from the equation given above. In the last column the absolute value is given under the provisional assumption $x = -0.75 \times 10^{-6}$ which number may be a number of per cent. false.

[1] The atomic weights are from those collected by the German Chemical Society (Chem. Ber., 31, p. 2761, 1898; Wied. Beibl., 23, pp. 69 und 315, 1899, whereby O = 16.00). The question as to the atomic weight of cobalt and nickel is still a subject of chemical discussion; compare Cl. Winkler, Zeitsch. anorg. Chem., 17, p. 236, 1898; Th. W. Richards and G. P. Baxter, l. c., 21, 251 and 22, p. 221, 1899; St. Meyer, Wied. Ann., 69, p. 263, 1899, hints at the possibility of an inverted order in the series.

[2] Recalculated according to the collection of W. Ostwald, Stoichiometrie, 2. Aufl., p. 512, Leipsig, 1891.

TABLE II.

Temperature 18°C. $x = -0.75 \times 10^{-6}$

	Name of Salt in Water Solution.	q	Formula.	O = 16.00		$\frac{M_w}{M_s}$	$-\frac{i_m}{x}$	$+i_m$
				a	m			
1	Chromium Sulphate.	3	$Cr_2(SO_4)_3$	52,1	392,38	40,73	2×7990	0,00599
2	Chromium Potass. Alum.	3	$CrK(SO_4)_2$	52,1	283,37	29,63	8400	0,00629
3	Chromium Amm. Alum.	3	$CrNH_4(SO_4)_2$	52,1	262,30	30,77	8070	0,00605
4	Chromium Nitrate.	3	$Cr(NO_3)_3$	52,1	238,22	35,28	8400	0,00629
5	Manganous Fluoride.	2	MnF_2	55,0	93,00	215,71	20060	0,01504
6	Manganous Chloride.	2	$MnCl_2$	55,0	125,90	163,10	20530	0,01540
7	Manganous Bromide.	2	$MnBr_2$	55,0	214.92	94,63	20340	0,01524
8	Manganous Iodide.	2	MnI_2	55,0	308,70	65,49	20220	0,01516
9	Manganous Sulphate.	2	$MnSO_4$	55,0	151,06	133,65	20190	0,01514
10	Manganous Ammon. Sul.	2	$Mn(NH_4)_2(SO_4)_2$	55,0	283,28	71,04	20130	0,01509
11	Manganous Nitrate.	2	$Mn(NO_3)_2$	55,0	179,08	114,37	20480	0,01536
12	Ferrous Iodide.	2	FeI_2	56,0	309,70	55,18	17090	0,01282
13	Ferrous Sulphate.	2	$FeSO_4$	56,0	152,06	111,72	16990	0,01272
14	Ferrous Ammon. Sul.	2	$Fe(NH_4)_2(SO_4)_2$	56,0	284,28	59,42	16890	0,01268
15	Ferric Chloride.	3	$FeCl_3$	56,0	162,35	111,14	18040	0,01356
16	Ferric Bromide.	3	$FeBr_3$	56,0	295,88	66,77	19750	0,01482
17	Ferric Sulphate.	3	$Fe_2(SO_4)_3$	56,0	400,18	101,06	2×20200	0,01515
18	Ferric Ammon. Alum.	3	$Fe(NH_4)(SO_4)_2$	56,0	266,20	75,64	20140	0,01510
19	Ferric Ammon. Oxalate.	3	$Fe(NH_4)(S_2O_4)_2$	56,0	250,08	81,75	20450	0,01533
20	Ferric Nitrate.	3	$Fe(NO_3)_3$	56,0	242,12	74,48	18030	0,01352
21	Cobaltous Fluoride.	2	CoF_2	59,0	97,00	142,60	13830	0,01037
22	Cobaltous Chloride.	2	$CoCl_2$	59,0	129,90	108,21	14060	0,01054
23	Cobaltous Bromide.	2	$CoBr_2$	59,0	218,92	63,13	13820	0,01036
24	Cobaltous Iodide.	2	CoI_2	59,0	312,70	44,08	13790	0,01034
25	Cobaltous Sulphate.	2	$CoSO_4$	59,0	155,06	87,65	13590	0,01019
26	Cobaltous Nitrate.	2	$Co(NO_3)_2$	59,0	183,08	76,62	14030	0,01052
27	Nickelous Fluoride.	2	NiF_2	58,7	96,70	61,50	5950	0,00446
28	Nickelous Chloride.	2	$NiCl_2$	58,7	129,60	46,02	5960	0,00447
29	Nickelous Bromide.	2	$NiBr_2$	58,7	218,62	27,00	5900	0,00442
30	Nickelous Iodide.	2	NiI_2	58,7	312,40	18,62	5820	0,00436
31	Nickelous Sulphate.	2	$NiSO_4$	58,7	154,76	37,39	5790	0,00435
32	Nickelous Nitrate.	2	$Ni(NO_3)_2$	58,7	182,78	32,31	5910	0,00443
33	Cupric Chloride.	2	$CuCl_2$	63,6	134,50	16,33	2200	0,00165
34	Cupric Bromide.	2	$CuBr_2$	63,6	223,52	9,40	2090	0,00157
35	Cupric Sulphate.	2	$CuSO_4$	63,6	159,66	13,72	2190	0,00164
36	Cupric Nitrate.	2	$Cu(NO_3)_2$	63,6	187,68	11,54	2170	0,00163

From the series of numbers in the foregoing table we may draw the following conclusions: The molecular susceptibility shows the well-known increase from chromium to manganese and iron and then a gradual decrease to copper. The four halogen salts could be investigated unobjectionably as bivalent salts only, in the case of manganese, cobalt and nickel; there occurs here again a regular increase from the fluoride to the chloride with a following decrease to the iodide. Simple additive or subtractive properties are obviously not present.

The approximate coincidence of the chlorides and nitrates is striking throughout; in connection with the ferric compounds it is noticeable that the bromides, sulphates, oxalates, give values which are 12 per cent. higher than those which the ferrous compounds furnish; this agrees with the results found by G. Wiedemann. Moreover, the difference among the separate salts amounts to 5 per cent., so that the introduction of a fixed atomic susceptibility for the cation cannot be allowed without considerable arbitrariness. That this quantity exerts by far the chief influence upon the value of the molecular susceptibility has, of course, never been doubted. We have investigated the sulphates of six metals. These are suitable for comparison with earlier observed values and with the proposed algebraic relations which are collected in Table III.

TABLE III.

Observer.	Cr'''	Mn''	Fe''	Fe'''	Co''	Ni''	Cu''
Liebknecht–Wills (from exp.)	7990	20190	16990	20200	13590	5790	2190
" " ($Ni''=a$)	1.38a	3.49a	2.93a	3.49a	2.35a	a	0.38a
" " ($b=1.25a$)	——	3.50a	2.88a	——	2.25a	a	——
G. Wiedemann (exp. $Ni''=a$)	1.34a	3.29a	2.74a	3.26a	2.26a	a	——
Jäger–Meyer: ($Ni''=a=b$)	——	3a	2.5a	——	2a	a	——

Our values for the sulphates of Mn, Fe, Co and Ni may be approximately represented by Wiedemann's proportion, whereby $b = 1.25a$; of course, only two of the latter numbers are independent since Mn and Ni serve to determine the parameters a and b; putting $a = b$ does not give an agreement with our results. Finally, these are with respect to nickel everywhere larger than

those of Wiedemann, also than those of Jäger and Meyer; the departure can only be explained in case the nickel compounds investigated by these observers should have contained cobalt; this, in our judgment, must have been the case.

We wish to thank Dr. W. Meyerhoffer for his kind assistance in carrying out numerous analyses. The investigations were carried out in the laboratory of Professor H. du Bois, to whom our cordial thanks are due.

BERLIN, December, 1899.

GIBBS' THERMODYNAMICAL MODEL.

BY W. P. BOYNTON.

IN Maxwell's Theory of Heat, p. 207, is a drawing showing some of the principal lines on a thermodynamical model, suggested by Professor J. Willard Gibbs, of Yale University. I have been told that Professor Maxwell had two of these models constructed, one of which remained at Cambridge, England, the other being sent to Professor Gibbs at Yale. There is also a copy of this model at Clarke University, Worcester, the only one which I have seen. While there may be others in existence, these are the only ones which I have known of, and I suspect that very few have ever been constructed.

This year, in connection with a course in thermodynamics, two of my pupils are attempting to construct one of these models, but are met by various serious difficulties, which may interest others.

In the diagram of which I speak, which is here reproduced, the directions chosen for the different coördinates are not immediately evident. Even by the aid of the description in the text I have not been able to locate them satisfactorily. In the attempt so to do, I have been guided by the following general considerations. Using Maxwell's notation, in which

v = volume.
p = pressure.
T = absolute temperature.
e = energy.
φ = entropy.

The equation relating these quantities is

$$Td\varphi = de + pdv$$

which transposed gives

$$de = Td\varphi - pdv = \frac{\partial e}{\partial \varphi} d\varphi + \frac{\partial e}{\partial v} dv$$

the differential equation of the thermodynamical surface of which the coördinates are the entropy, volume and energy, and whose slope at each point in the principal directions gives the temperature and pressure, by the identities

$$T = \frac{\partial e}{\partial \varphi}, \quad p = -\frac{\partial e}{\partial v}.$$

These are subject to the conditions that T is always positive, and p

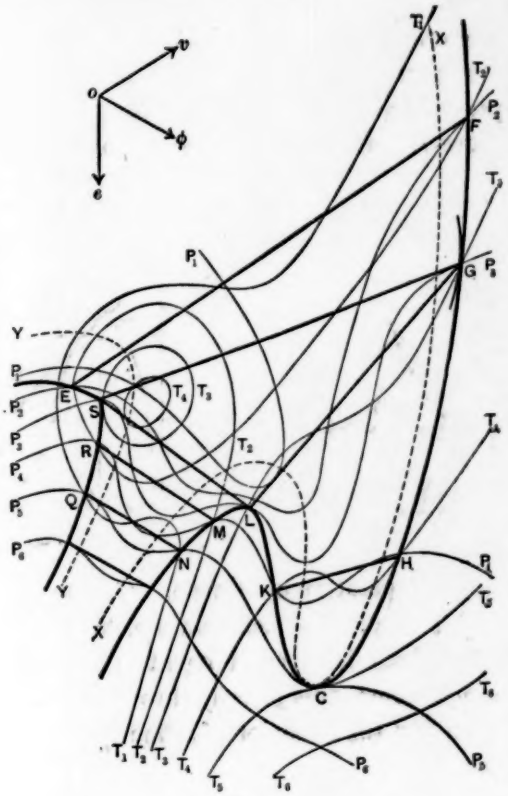


Fig. 1.

is usually positive, always so for the gaseous state, usually for the liquid and solid states.

If then e is taken vertically downward and v and φ horizontal, passing along a section of the surface by a plane of constant volume, in the direction of increasing entropy the slope will always be

downward, and generally convex, as the addition of heat, that is energy to a substance at constant volume increases its entropy, and generally its temperature, never decreasing it. A section by a plane of constant entropy will have a slope in the direction of increasing volume which is in general upward, corresponding to a positive pressure, and in all parts of the model referring to stable states of the substance this will be convex, since increase of volume is then accompanied by decrease of pressure.

I have attempted to determine the choice of coördinates by the properties of the critical state. In the two diagrams the broken line separates the parts representing stable or homogeneous states from parts representing unstable or non-homogeneous states.

In the pressure-volume diagram lines of constant pressure, vol-

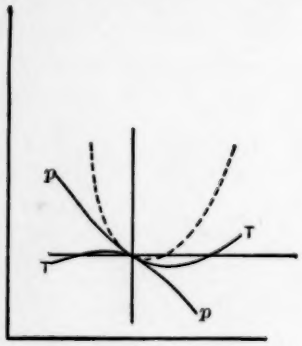


Fig. 2.

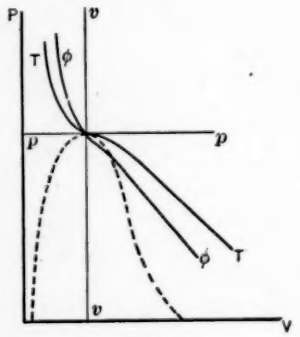


Fig. 3.

ume, entropy and temperature are drawn. On the other are drawn lines of constant pressure and temperature, taken from Maxwell. In both diagrams these lines are tangent to the broken line. In Fig. 2, the line $v = \text{const.}$ cuts sharply through the broken line. I have attempted to find the behavior of a line of constant entropy in the following way :

For a substance following van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

the equation of an isentropic can be shown to be

$$\left(p + \frac{a}{v^2}\right)(v - b)^k = \text{const.}$$

where k is the ratio of the specific heats at constant pressure and constant volume. The slope of this curve is found to be

$$\frac{dp}{dv} = \frac{2a}{v^3} - \frac{k\left(p + \frac{a}{v^2}\right)}{v - b},$$

which becomes, substituting the values of the critical pressure and volume

$$\left(\frac{dp}{dv}\right)_{\text{crit.}} = \frac{2a(1-k)}{27b^3};$$

which is negative for real positive values of a and b. Hence the isentropic appears also to cut through the broken line, but less sharply.

Still further, we believe that the line of constant volume does not again cut out of this non-homogeneous or unstable area, while the isentropic may. Hence it has seemed to me necessary to consider the vertical line of Fig. 3 a line of constant volume, and the

Fig. 4.

horizontal line an isentropic, while the critical point lies a little to the left of the vertex of the curve, so that the isentropic slightly cuts through the broken line.

The choice of coördinates will then be, energy, vertically downward, in the three-dimensional model, volume, measured to the right, in the diagram, Fig. 1, and entropy vertically downward, in the same diagram. This choice is not inconsistent with the arrows in the upper left-hand corner of Fig. 1. The model which has been

constructed in accordance with these considerations is shown in the accompanying figure.

It satisfies the general requirements as to slope and convexity. It represents the gaseous or vapor state as having in general the greatest volume and a great range of pressure, etc. One property, however, does not seem to be indicated by this model, nor do I see how to satisfactorily change it so that this can be done.

It has been deduced mathematically and shown experimentally that if a saturated vapor be expanded adiabatically, or isentropically, it may either become superheated or partially condense to liquid; in fact both phenomena can be shown with one substance, as for instance, chloroform above 127° C. becomes superheated, and below this temperature condenses, by sudden expansion, while at this temperature no visible effect is produced by either expansion or compression. That is, there is an isentropic which is at a particular point tangent to the "steam line," those on one side of it not touching it at all, while those on the other cut both in and out. This particular property is not shown by the model as constructed, with the present choice of coördinates. If, however, we had measured entropy horizontally in Fig. 1, then the isentropics, being vertical, might be tangent to, or cut through the steam line. This choice of coördinates has, however, seemed impossible for the reasons previously given.

We may, if we wish, discuss the question by a different method. The lines drawn in Figs. 1, 2 and 3 are all lines through the critical point. In Fig 2 the lines of constant pressure and temperature are tangent to the broken line; Fig. 3 shows the same property. In Fig. 2 the line of constant entropy cuts the broken line twice, but no other pair of lines has more than one intersection. Fig. 3 does not, as drawn, show the same property. In Fig. 2, passing from the water-line around the critical point in the homogeneous region to the steam-line, one cuts the lines in the following order: water-line, pressure, temperature, entropy, volume, pressure, temperature, entropy, steam-line. Fig. 3 gives the same order, with the choice of coördinates which we have adopted, if we let the temperature lines always slope downwards as due the pressure lines. With this change the two diagrams seem to agree, but otherwise their disagreement seems hopeless.

I shall be very glad to receive from anyone any suggestion which will help to remove the apparent disagreement between the two diagrams, or so modify the model that it may more completely represent the possible properties of actual bodies than it now seems to do.

THE UNIVERSITY OF CALIFORNIA, BERKELEY, CAL., Feb. 1, 1900.

ON THE TEMPERATURE OF THE ACETYLENE FLAME.[1]

BY EDWARD L. NICHOLS.

CONCERNING the temperature of the acetylene flame, varying and incompatible statements are in existence. The temperature of combustion of this gas, according to Le Chatelier,[2] would be, when burned in air, from 2100° to 2420°. Measurements with Le Chatelier's pyrometer, on the other hand, made by V. B. Lewes,[3] gave temperatures lower than those of ordinary gas flames. Lewes found for the obscure zone 459°, for the edge of the luminous zone 1411°, and for the region near the summit of the luminous zone 1517°. Smithells,[4] upon the appearance of the data given by Lewes, described a series of experiments for the purpose of showing that the temperature of the flame is, in point of fact, very much higher than the values given by that author and that in many portions it is higher than the melting point of platinum.

It can be easily shown by inserting wires of that metal into the flat acetylene flame obtained from any one of the forms of burner usually employed, that while the thicker wires remain unmelted, those of very small diameter are readily fused. I found, for example, that a wire having a diameter of 0.0082 cm. became fused at the end with the formation of a distinct globule, before the metal had penetrated the outer luminous layer of the flame, whereas wires of 0.01 cm. or larger diameter remained unmelted. The experiments of Waggener, cited by St. John,[5] show that there are portions of the flame of the Bunsen burner in which it is possible to melt platinum, while MacCrae,[6] working with a platinum-rhodium

[1] A paper read at the meeting of the American Physical Society, February 24, 1900.
[2] Le Chatelier, Comptes Rendus, 121, p. 1144 (1895).
[3] Lewes, Chem. News, 71, p. 181 (1895).
[4] Smithells, Journal of the Chemical Society, 67, p. 1050 (1895).
[5] St. John, Wiedemann's Annalen, 56, p. 434 (1895).
[6] MacCrae, Wiedemann's Annalen, 55, p. 97.

element found for the hottest region in the Bunsen flame 1725°. It will be seen from the experiments to be described in this paper that MacCrae's determination, which was made with wires having a diameter of 0.02 cm. is not incompatible with the observations of Waggener and others. Smithells, in the paper just cited, describes the melting of platinum wires having a diameter of 0.01 cm. in various parts of the outer sheath of a flat flame of illuminating gas.

Pellissier[1] in commenting upon Lewes's measurements refers to experiments in which minute wires of platinum, made by Wollaston's method of silver plating, drawing and subsequent dissolving of the silver coating, when thrust into the flame of a candle, melted instantly. I have not been able to find other printed reference to these observations and do not know with whom they originated. An attempt to repeat the experiment with a Wollaston wire resulted in the ready fusion of the wire by the flame. An examination of the remaining portions under the microscope showed that the metal had been melted down into clean well-rounded beads, and had not been consumed by oxidation or any other chemical reaction.

It will appear from the experiments to be described in this paper that Smithell's contention that the temperature of flames cannot be obtained directly from the indications of a thermo-element, for the reason that such an element loses heat by conduction and by dispersion from its surfaces so that the portions submerged in the flame never arrive at the temperature of the surrounding gases, is well founded. Lewes recognized this fact, and in his measurements made use of wires of three different sizes.

The Apparatus.

It is obvious that the indications of a thermo-couple which is submerged in a flame must depend upon the diameter of the wire, and it is upon this fact that my method for the estimation of the temperature of the acetylene flame is based. The flame selected for these measurements was of the usual flat type, obtained by the impinging of two jets of acetylene properly mixed with air, which issued from the orifices of one of the well-known forms of acetylene gas burner. The burner was mounted on a stand sliding upon a

[1] Pellissier; l'Eclairage a l'acétylène (Paris, 1897), p. 186.

horizontal steel bar, so that a free lateral motion could be given to the flame. This stand moved so smoothly upon its metal support that the flame could be shifted by the direct action of the fingers of the operator with the same precision and freedom that we find in the well-adjusted draw tube of a microscope; and lateral displacements of about 0.01 cm., or even less could be made with ease. In some of the experiments requiring more accurate control, the flame was moved by means of a fine micrometer screw clamped to the bar. Upon a similar stand, attached to the same bar, was mounted one of the series of thermo-elements by means of which the determinations in question were to be made. The wires were all drawn from the same samples of pure platinum and platinum-rhodium (10%), obtained from Heraeus in Hanau, from stock believed to be identical with that tested by Holborn and Wien.[1] That thermo-elements made of wires differing in diameter, but all from the same stock, give with sufficient accuracy identical results, has been abundantly established. The hot junctions were given the form

Fig. 1.

shown in Fig. 1. The platinum and platinum-rhodium wires were fastened by sealing into the fused ends of an open glass rod about 10 cm. in length, and 1 cm. in diameter, and the free ends of these wires were cut off, leaving about 3 cm. extending beyond the glass. These ends were pinched together in the form of a V, and while in contact were fused by a brief immersion in the oxy-hydrogen flame. The junction thus formed was trimmed off at right angles to the axis of the tube, until the thickness of the fused portion joining the two wires was as small as could be obtained without danger of rupturing the junction. It was found that by this process of trimming away with a pair of pocket scissors, better results could be obtained than by the use of file, or emery

[1] Wiedemann's Annalen, 47, 107, and 56, 360.

paper, and that the preparation of junctions in this way was very easy and expeditious. It was almost always possible, after a few trials, to secure a junction in which the thickness of the connecting link of fused metal would not exceed 0.005 cm.

When viewed under the microscope, a junction thus prepared presents the appearance shown in Fig. 2. The surface left by trimming is smooth, and lies in a plane at right angles to the axis of the tube in which the wires of the thermo-element are mounted. When such a junction is brought near to the flat flame from an acetylene burner, its plane face lies parallel to the sheaths or layers of which the flame is composed and it is true, with a high degree of approximation, that the whole of the junction is in a surface of equal temperature.

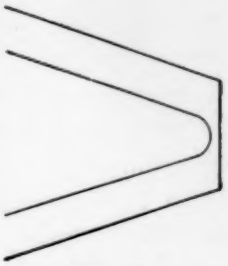


Fig. 2.

The electromotive force produced by the heating of the thermo-element in the flame was measured by means of a potentiometer consisting of a sensitive galvanometer of the D'Arsonval type and an accurately adjusted resistance box containing coils ranging from 50,000 ohms to 1 ohm. A large Clark cell of the old Feussner type was mounted in series with the resistance box. The thermo-element, the galvanometer, and a subsidiary resistance of 10,000 ohms were looped around a portion of the resistance box, the ratios being varied according to the Poggendorff method until complete balance was secured. The electrical connections are shown in Fig. 3. The type of standard cell selected for this work is subject to considerable errors from diffusion lag. It has, however, the advantage of being capable of furnishing a much larger amount of current than the small types of cell in which diffusion lag is avoided,

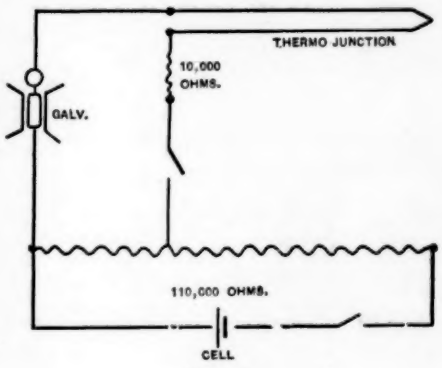


Fig. 3.

without appreciable loss of electromotive force. Two of these cells were placed side by side in a thick-walled inner room which had been constructed for the purpose of securing uniform temperature for the standard clock of the physical laboratory, and other similar apparatus. The range of temperature in this room fluctuated throughout the entire investigation between 18°C. and 19°C. The range was so small and the variations occurred so gradually that no changes of electromotive force of a size which it was necessary to consider in these measurements could have risen, other than those included in the usual correction for temperature.

The two cells were compared with each other from time to time by setting them in opposition to one another in circuit with a sensitive galvanometer and noting the deflection produced. It was found that although one of them was supplying current to the 100,000-ohm circuit of the potentiometer, during the times when it was necessary to close the key of that circuit, the difference of electromotive force between the used and unused cell was always very small, never more than a few hundred thousandths of a volt. At the end of the entire set of measurements, the difference was 0.00006 volt. The absolute electromotive force of these cells was checked by comparison with Clark cells of the H form and of the test-tube form, constructed in this department in 1898. As a result of these comparisons, it was found that the electromotive force of the cell used in the potentiometer might be taken at 1.430 volts at 18°.

For the convenient observation of the acetylene flame and of the distance from the median plane of that flame to the junction of the thermo-element, a long micro-camera was employed, the distance from the lens of which to the ground glass plate was about two meters. By means of a projecting lens of long focus, which was substituted for the ordinary photographic lens usually employed in this camera, an image of the flame and thermo-junction, enlarged to about seven diameters, was projected upon the ground glass. The plane of the flame was parallel to the axis of the camera so that those portions of the image of the former that were in focus were seen as if in cross section.

The stream of acetylene and air issuing at right angles to each

other from the openings in the lava jet when viewed in the image, presented the appearance of cylinders or tubes with luminous walls, which under ordinary pressures united after meeting into a single stream of gas, the walls of which were very sharply defined and bright. Outside of this, and swaying back and forth with the drafts of air to which the flame is subjected, was an ill-defined image of the wings of the flame which consist of portions of the gaseous envelope which have lost their velocity and in consequence, the remarkable ability to resist deformation, possessed by the body of the flame. The thickness of the stable portion of the flame, which is surrounded by a well-defined luminous layer was found to be about 0.065 cm. The walls of brilliantly incandescent material around this central body were not more than 0.005 cm. in thickness. The appearance of these essential portions of the image of the flame on the ground glass is shown in Fig. 4, which is an outline sketch from a photograph of the flame. It will be noted that the body of the flame is not vertical, which arises from the fact that one of the jets is slightly stronger than the other. On account of the smallness of the openings in an acetylene burner, it is rare to find complete symmetry in these jets. The flame is almost always slightly thrown to one side as shown in the drawing, one face being convex, the other concave. These slight defects from symmetry do not in any way interfere with the measurement of the flame temperature.

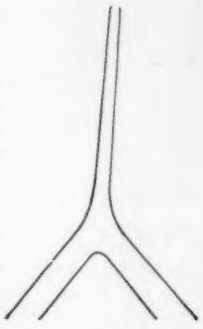


Fig. 4.

Measurements of the Acetylene Flame.

The wires selected for the four junctions to be used in the experiment upon the acetylene flame were measured under a microscope with micrometer stage. Their diameters were as follows:

Table I.

Junction	I.	Diameter	0.01996 cm.
"	II.	"	0.01598 "
"	III.	"	0.01089 "
"	IV.	"	0.00821 "

Readings were first made with junction I (diameter 0.01996 cm.). The flame was set at a distance of 6 mm. from the face of the junction and the potentiometer was balanced. The flame was then moved stepwise nearer and nearer, and the potentiometer rebalanced at each step until the face of the junction coincided with the edge of the luminous mantle at a point just above the apex of the inner non-luminous zone. (See *x*, Fig. 5.)

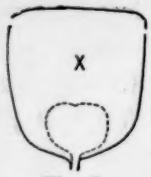


Fig. 5.

The rise of temperature indicated by the potentiometer readings is shown in curve *a* (Fig. 6), the data for which as well as for the other curves in that figure are contained in Table II. The increase of temperature is gradual at first, but at a distance of about 0.4 cm. from the center of the flame, the curve suddenly becomes steep. It is probable that this distance measures the thickness of the layer of non-luminous gas which surrounds the visible flame. Outside of this region the junction is heated almost altogether by radiation. As soon as it penetrates the column of moving gas, however, heat is brought to it principally by convection. Before the surface of the luminous mantle is reached the curve shows indications of approaching a maximum.

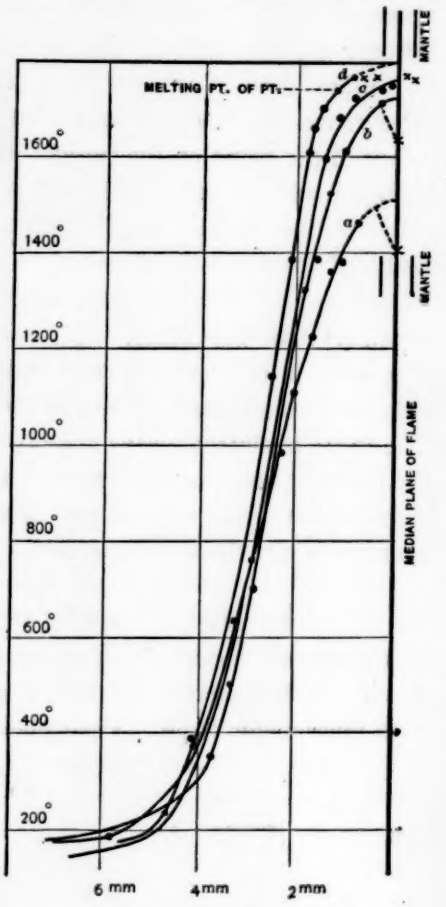


Fig. 6.

Upon pushing the flame still nearer to the junction, so that the latter penetrated the luminous region, an accumulation of lampblack began to form upon the wire, with fall of temperature. This proc-

ess in the case of acetylene is so rapid that at the end of two minutes a button of carbon several millimeters in diameter is formed.

TABLE II.

Temperatures indicated by thermo-junctions I, II, III and IV, at various distances from the median plane of the acetylene flame.

Junction I.		Junction II.		Junction III.		Junction IV.	
Distance.	Temp.	Distance.	Temp.	Distance.	Temp.	Distance.	Temp.
mm.		mm.		mm.		mm.	
5.62	185°	——	——	5.42	165°	4.63	233°
3.91	370°	3.65	353°	4.82	183°	4.11	406°
2.85	760°	3.33	508°	3.21	657°	2.55	1168°
2.09	1128°	2.90	695°	2.03	1278°	2.12	1411°
1.66	1229°	2.30	989°	1.50	1598°	1.86	1613°
1.30	1367°	1.93	1322°	1.18	1685°	1.70	1667°
1.07	1382°	1.68	1385°	0.894	1724°	1.54	1705°
0.850	1467°	1.40	1513°	0.566	1747°	1.30	1738°
		1.09	1617°	0.238	1759°	1.025	1771°
		0.320	1715°	0.00	1775°	0.780	molten
				−0.29	molten	0.300	molten

This is finally torn loose from the wire by its own weight; whereupon the deposition of a new mass begins. I attempted, by watching the breaking away of the carbon from the wire, which occurred at regular intervals, to determine the temperature of the wire before the coating of carbon had begun to show itself again. The highest temperature which it was possible to observe in this way was nearly one hundred degrees below that in the luminous layer, and it was obvious from the movement of the galvanometer needle that the junction was being rapidly cooled.

Junction II. (diameter 0.01598 cm.) was now substituted for junction I., and a similar set of readings were made. This junction, as had been anticipated, showed higher temperatures. It was found possible, owing to the small diameter and consequently high temperature of the wire, to penetrate further into the flame before the deposition of carbon began; so that measurements with the junction actually within the luminous layer could be made. The general form of the curve, as will be seen by inspection of the figure (curve *b*) is the same as that obtained with junction I. After penetrating the luminous mantle to a small fraction of a millimeter,

carbon began to gather upon this junction likewise, with lowering of temperature as in the case of junction I. The attempt to read temperatures immediately after the dropping of the accumulated carbon showed that the highest temperature which could thus be observed was again about one hundred degrees below the temperature of the luminous mantle. It was clear in this case, as before, from the rapid fall of temperature already going on, that this reading has no significance.

Similar readings with junction III. (diameter 0.0108 cm.) gave a third curve of the same type as those plotted from the readings made with I. and II.; but the temperatures were higher throughout. With this junction, it was found possible to penetrate to the center of the flame without the deposition of carbon, the temperature of the wire being apparently too high to permit the formation of soot. Upon pushing through the median plane of the flame to the second luminous mantle the junction was melted. This result was not unexpected, since the temperature of the junction at the first luminous mantle reached 1750°, so that a rise of twenty-five degrees of temperature would suffice to produce fusion. The wire when pushed through the flame in the manner just described is heated for greater and greater distances back from the junction until the losses of heat at the junction are sufficiently diminished to raise the tips of the wires to the melting-point.

With junction IV. (diameter 0.0082 cm.) a fourth curve, similar in form to the preceding ones and with still higher temperatures was obtained. This junction was fused at a distance of 0.075 cm. from the core of the flame, and of 0.037 cm. from the edge of the first luminous mantle. It was easy to observe in the enlarged image upon the plate of the micro-camera, the melting away of the platinum wire, while the platinum-rhodium alloy was still unaffected, and while contact was still unbroken. A satisfactory observation of the electromotive force of the thermo-element at the melting-point of platinum was thus obtained. This reading (0.018236 volt) differs from the value found in my calibration of the thermo-junctions used in this investigation (0.018262 volt) by a quantity (0.000026 volt) less than the errors due to changes in the electromotive force of the standard cell. If the latter reading be taken to correspond to 1775° the former indicates 1773°.

Beyond this point it was impossible to make direct observations of temperature; but the form of this and the preceding curves were so closely allied that I felt no hesitation in extending the curve *d* to the core of the flame. This has been done by means of dotted lines in the figure. Curves *a* and *b* have been extended in the same manner. In order to form an estimate of the temperature which would have been reached by a thermo-junction of negligible cross-section, provided such a junction could have been obtained which was capable of registering temperatures above that of the melting point of platinum, the ordinates of the four curves *a*, *b*, *c* and *d* were taken for the core of the flame, for the plane of the luminous mantle, for a plane distant 0.07 cm. from the core, and for a plane 0.10 cm. from the core. These readings were plotted

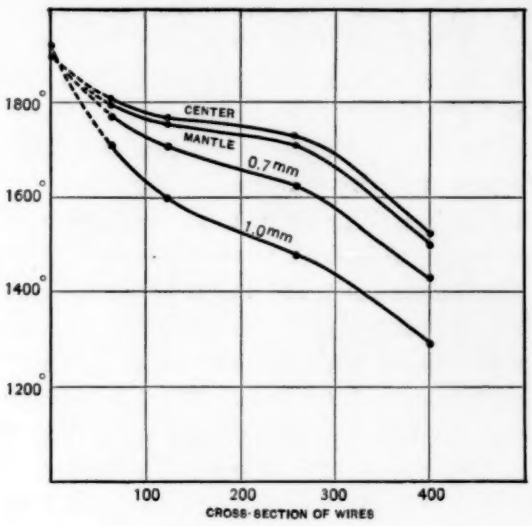


Fig. 7.

and curves were drawn through them as shown in Fig. 7; relative cross-sections of the wires being taken as abscissæ, the temperatures as ordinates. If these curves could be extended to the line representing zero cross-section, the temperatures indicated by the points in which each of them cuts that line would give the temperature of the portion of the flame to which the curve corresponds. There is a considerable element of uncertainty in extrapolation even

over so short a range as this; but it is obvious from the character of the curves lying within the limits of observation that each of them trends upward and it seems highly probable that they all meet the line of zero cross-section at a temperature not far from 1900°. The fact that the curves cut this line at nearly the same temperature would seem to indicate that the distribution of temperatures from the center of the flame outward for a distance of about 1 mm. is a nearly uniform one.

It would, perhaps, be unwise to attempt to draw any more definite conclusion from the probable trend of these curves; but I have ventured to extend them in the manner shown in the figure, so that the curve for the region 1 mm. from the center of the flame reaches the zero of abscissæ about twenty degrees above that for the center of the flame, *i. e.*, at 1920° and the intermediate curves at temperatures lying between. I regard this as an extreme treatment of the case, and allude to it only to indicate that, in accordance with common belief, the highest temperature may be found in the outer non-luminous layer of the flame; but that it is unlikely that the difference amounts to more than twenty degrees.

The point of intersection referred to above lies more than one hundred degrees above the highest temperature recorded by even the smallest of the thermo-elements, and it is safe to infer that nearly all previous attempts at the measurement of flame temperatures must, for lack of correction of the error, due to loss of heat through the wire, be regarded as much too low. The Junction IV. is, so far as I am aware, the smallest in cross section that has been used in such work. With larger wires, the correction for loss of heat would be even greater, except in cases where, as in the observations made by Smithells, pains were taken to immerse an extended portion of the wires within the flame.

TEMPERATURE OF OTHER FLAMES.

For the purpose of comparison, I measured in a manner analagous to that just described, the temperature of the luminous flame of ordinary illuminating gas, and the flame of a candle. The gas flame employed for this purpose was obtained from a lava tip, rated at one cubic foot and giving a flat flame of the usual form. The

image of this flame, when viewed upon the ground-glass screen of my camera was found to be comparatively ill-defined and unsteady; but although the outlines of the luminous sheath were much less clearly marked than in the case of the acetylene flame, they were discernible. Owing to the continued motion, due to the small velocity of the gas issuing from the jet, no attempts were made to plot curves of temperatures outside the flame. All readings were made with the junction as nearly as possible in contact with the outer surface of the luminous sheath, at a point in the brightest portion of the flame. This position is approximately in dicated by the letter x in Fig. 8. The four junctions already described were mounted, one after another, in such a position that the flame could be moved up until they came into contact with the sheath at the point indicated. The temperatures of the junctions when in that positiona are given in the following table:

Fig. 8.

TABLE III.

Junction I.	1385°
Junction II.	1484°
Junction III.	1609°
Junction IV.	1676°

These values having been plotted with relative cross sections of the wires as abscissæ, and temperatures as ordinates were found to lie upon a smooth curve (g) as shown in Fig. 9. This curve when extended to the line corresponding to zero cross section gave for the temperature of the flame 1780°, a temperature sufficient to account for the success of Smithells's experiment, already described, in which platinum wires of small diameter were melted in the outer sheath of such a flame. I found it easy, by holding a wire of the size used in junction IV. in a plane parallel to that of the flame, and moving it gradually toward the latter, to verify his statement. The wire was readily melted.

It was not thought necessary to make further experiments upon this flame. The region selected was, so far as one could judge from the brightness of the luminous sheath, the hottest portion of the

flame. My measurements upon this region would lead to the conclusion that *the luminous sheath of ordinary gas flames is at least one hundred and twenty degrees lower than the corresponding region in the acetylene flame.* Luminous flames of ordinary illuminating gas would perhaps repay further study, but owing to the fact that such

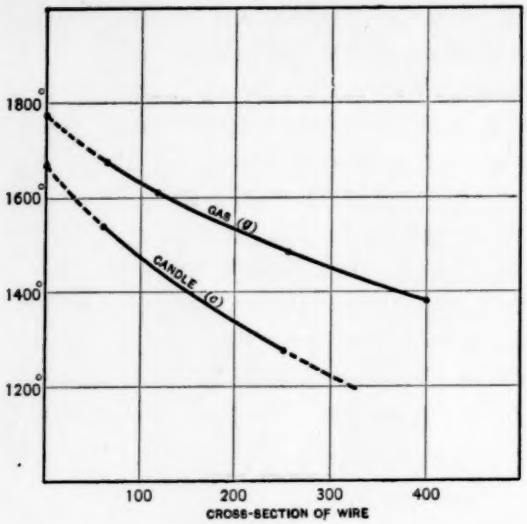


Fig. 9.

gas is an ever-varying mixture and that it is burned under conditions of pressure, etc., such as to give a fluctuating character to the flame, the problem would have at best an indefinite character from which studies of the acetylene flame are free. In the latter case we have to deal with a definite fuel and the velocity of the jets of gas from the burner is sufficient to give a high degree of stability.

The candle would seem an even less satisfactory subject of study in these respects than illuminating gas, but the fact of the melting down of Wollaston wire in a candle flame, the verification of which I have briefly described in the opening paragraphs of this paper, seemed to discredit so completely the lower values commonly assigned to the temperature of such flames that I decided upon a redetermination.

The fact that the flame of a candle, mounted upon a fixed stand, would move steadily downward as the material of which it was com-

posed burned away, made it convenient without any serious modifications of my apparatus, to explore the temperature of the luminous sheath throughout the entire length of the flame. It was only necessary for this purpose to mount a candle upon the steel bar in the position previously occupied by the acetylene flame and when it had reached such a length that the level of the rim of the cup lay below the level of the junction, to move the candle toward the latter by means of a micrometer screw until the junction began to be submerged in the luminous sheath of the flame. It was then easy by a series of slight adjustments of the flame, to explore with the junction the entire surface of the luminous sheath from base to tip, measuring temperatures from time to time, and determining the position by means of the height of the junction above the rim of candle cup. The latter observations were readily made by means of the image of the candle upon the ground glass of the camera. Explorations of the candle flame in the manner described were made with junctions II. and IV. and the results obtained showed a degree of consistency much greater than the fluctuating character of the source under observation had led me to expect. Both sets of observations showed a maximum of temperature in the same region; that lying just above the tip of the interior dark zone of the flame. Readings were made by watching the movements of the candle flame and securing a balance of the potentiometer at times when the face of the junction was as nearly as possible in contact with, but not deeply submerged within the luminous layer. Whenever the wire plunged to any considerable depth beyond the luminous surface, deposition of soot occurred with lowering temperature, and it was necessary to withdraw it into the non-luminous regions outside and to wait until the deposit had been burned off, before proceeding with the readings. In computing the actual temperatures of the luminous sheath of the flame from these readings, I contented myself with the following rough approximation. The maximum temperatures shown by junctions II. and IV. were plotted upon the same diagram used for the luminous gas flame. These temperatures were 1281° and 1546°; values which, as will be seen by inspection of Fig. 9 (*c*), lie much below those of the corresponding readings for the luminous gas flame, but in such positions as to make it easily possible to draw

through them a curve analagous in form to that obtained for the latter. Such a curve would cut the line of zero cross section at about 1670° which may, I believe, be taken as the approximate temperature of the hottest portions of the luminous sheath of the candle flame. Estimates of this temperature by the probably less accurate methods of drawing a straight line through the points in question and taking the points in which this line cuts the line of zero cross section to be the temperature of the flame, and estimates based upon the assumption that the true temperature is as many degrees above the temperature indicated by junction IV. for the candle as it is for the gas flame, would lead to values respectively twenty-four degrees and forty degrees lower than that obtained by the method which I have adopted. I believe that the temperature just given (1670°) is much closer to the truth than that obtained under either of the other assumptions. Estimated temperatures for other portions of the luminous sheath were made by assuming that the correction to be applied to the readings obtained with junction IV. would be the same in all positions. These values are given in Fig. 10 which may serve in place of an ordinary table. The portions of the flame to which each reading refers are more readily indicated by giving such a diagram of the flame than in any other way.

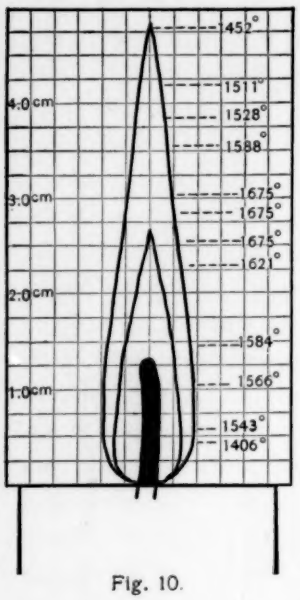


Fig. 10.

The fact that, in the case of the acetylene flame and the ordinary gas flame, this method gives values high enough to account for the melting of platinum, but leads to an estimate of the temperature of the candle flame which is about one hundred degrees below the melting point of that metal, would seem, at first sight, to throw the procedure into serious doubt. My experience with the method has, however, been such as to make an error of one hundred degrees in the estimation of the candle-flame temperature seem highly improb-

able. Messrs. Lummer and Pringsheim in a recent communication to the German Physical Society[1] give an estimate of the temperature of candle flames based upon a relation which they have established between the position of the maximum in the energy curve of the spectrum of a source of light and its temperature. Assuming the the radiating substance in the flame to have the properties of a *black body* they find this temperature in the case of the candle flame to be 1687°, a value but seventeen degrees above that which I have given.

To account for the fusion of Wollaston wire in the flame of a candle, one might consider the possibility of the existence in such a flame of layers of gas the temperature of which is much above the surrounding regions, and that these layers may be so thin that it would not be possible to submerge the thermo-junction completely in them. In such a case, the junction would give a value approximate to the average of the temperatures of the gases with which it was brought into contact. Before assuming this structure of the flame, which really has nothing to support it save the necessity of accounting for the apparent discrepancy which I have just pointed out, it seemed wise to consider, on the other hand, whether the melting point of the Wollaston wire was necessarily that of pure platinum. Such wires would be made of ordinary commercial metal, the melting-point of which might vary considerably from that of the purer platinum used in the determination of the temperature of fusion. It is likewise readily conceivable that in the process of drawing within the silver coating, a certain amount of silver might be worked into the pores of the platinum and not removed by the subsequent action of the nitric acid. The determination of the melting-point of even such minute wires is fortunately a simple matter by means of the form of thermo-element used in the experiments which I have just described. It is only necessary to wrap a piece of the wire to be tested around the junction as shown in Fig. 11, to cut it off so that the ends of the loop extend slightly (about 0.05 cm.) beyond the face of the junction ; and having mounted the junction in the usual manner, to move the acetylene flame up to it

[1] Lummer and Pringsheim ; Verhandlungen der Deutschen Physikalischen Gesellschaft ; 1899, p. 214.

by means of a micrometer screw, watching the enlarged image of junction and flame upon the ground glass of the micro-camera. The wire will then begin to fuse at its outer end, and the fusion, following upon the progressive movement of the flame, can be watched until the loop is melted back to the surface of the junction itself. With such precision can this progressive melting of the wire be carried out in a room free from draughts, that it is possible to melt away the loop of wire in front of the junction until no part of it protrudes beyond the smooth face of the latter, and yet leave that portion of the loop which extends behind the wire of the junction and is protected by it, unmelted. I performed this experiment with a piece of the same Wollaston wire which I had succeded in melting in the candle flame; and I found its melting point, as indicated by the electromotive force of the junction, to be 1674°. To test the question whether this very low melting-point was due to the presence of silver undissolved by the nitric acid, a piece of the same wire was left in the acid for twelve hours, after which the melting-point was again tested in the manner just described. The result of this determination was 1687°. The latter reading was, I think, too high, since subsequent examination under the microscope showed that the loop of the wire behind the junction had been melted, so that the junction was probably a few degrees too hot. At any rate, it may safely be concluded from these determinations that the melting point of the Wollaston wire was at least one hundred degrees lower than that of pure platinum, and that the fusion of such wire in the candle flame did not necessarily indicate that my estimate of the temperature of the flame was at fault.

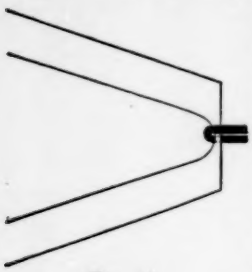


Fig. 11.

This point I deemed it worth while to confirm by direct observation of the melting-point of the Heraeus platinum; for which purpose a piece of the wire used in junction IV. was rolled into a flat strip. From this strip a piece about 0.01 cm. broad was cut, which was looped around the junction in the manner just described. The melting-point was found to be 1775°. Experiments upon the fusion of gold, platinum, palladium and other metals made in this way,

have convinced me abundantly of the delicacy and reliability of this means of determining melting-points. It is free from many of the most serious difficulties involved in the procedures usually employed. The details of this method, which is especially applicable to the calibration of thermo-elements, I propose to describe at some length under a separate title.

Scale of Temperatures.

The temperatures given in this paper are based upon a scale arbitrarily adopted, in which the melting-point of pure platinum is taken at 1775°, and gold at 1070°. Nothing more is claimed for this scale than that the reference points are those most easily reproducible in high temperature work, so that any one having occasion to use the data given can make reductions to whatever scale of temperatures he desires to employ. Up to the present time, high temperature work has not reached a stage in which it is possible to do more than to refer readings to these melting-points. The assignment of the proper degrees centigrade to the melting-points of gold and platinum appears as yet to be a somewhat uncertain matter, but the behavior of platinum—platinum-rhodium thermo-elements appears to be in so far consistent, that when the temperatures of these two points are fixed, but little doubt need be felt concerning the relative values of the intervening temperatures. Various wires even from the same maker will give electromotive forces that differ slightly one from another, but in general it may be said that with pure platinum—platinum-rhodium (10%) elements from a given stock of metal, the character of the curve will always be closely the same. Since my materials were from the same source as those used by Holborn and Wien, I have contented myself with the use of their curve, merely shifting the ordinates so as to make it pass through the points corresponding to the electromotive forces at the melting-points of gold and platinum as determined by myself. Various calibrations made in the course of other work appear to justify this procedure. These calibrations I hope to discuss at considerable length in a forthcoming paper. Whatever changes it may in future be found necessary to make in the assignment of these

fixed points can readily be extended to all my data, by any one who may care to do so.

To Mr. L. W. Hartman, who aided me in making many of the observations described in this paper, I desire to express my indebtedness.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, February 21, 1900.

NOTE ON THE LAW OF DISTRIBUTION OF VELOCITIES AMONG GAS MOLECULES.

By N. D. C. Hodges.

LET us consider one molecule. Let this molecule pass from a point A, to a point B, the time of passing being such that the molecule shall have come in contact with as many molecules as there are in the unit of volume. By taking a unit of volume large enough, the molecule considered will, when it reaches B, have passed through all possible velocities, and through each velocity in proportion to the frequency of that velocity among the molecules, *i. e.*, according to the law of distribution, if such exists.

The system consisting of the single molecule and all the other molecules is a conservative system. The sum of the kinetic energy of the single molecule and that of all the others, remains constant. The principle of least action applies.

Any particular velocity being represented by c, the number of times the molecule will have a velocity between c and $c + dc$ in passing from A to B, will depend on N, the total number of molecules in unit of volume, on some function of c, $\varphi(c)$, the form of which is to be determined, on dc, and on a constant A dependent on the temperature of the gas and the molecular weight.

The kinetic energy at any instant will be expressed by $ANc^2\varphi(c)dc$ and the action by $AN\int_0^\infty c^2\varphi(c)dc$.

That this may be a minimum, $\varphi(c)$ must have the form $\frac{\sqrt{h}}{\sqrt{\pi}}e^{-hc^2}$.

Hence the expression for the action becomes

$$\frac{AN\sqrt{h}}{\sqrt{\pi}}\int_0^\infty c^2e^{-hc^2}dc.$$

As the variation in the action due to changes of temperature is involvde in A, this expression is solely dependent on the number of velocities the molecule passes through, *i. e.*, it equals N. $\therefore A = 4h$. And the law of distribution is

$$\frac{4Nh^{\frac{3}{2}}}{\sqrt{\pi}}e^{-hc^2}c^2dc.$$

Harvard University, Cambridge, Mass.

NEW BOOKS.

The Elements of Physics. By HENRY CREW, PH. D. Pp. xiv + 347. The Macmillan Co., New York, 1899.

It is not often that the reading of an elementary text-book of physics can be referred to as distinctly refreshing, and yet in the case under consideration this is exactly true. The author writes in so lively a style, with so much enthusiasm for the subject, and with so appreciative a recognition of the value of the experience that the average boy has at his disposal in beginning the study of physics, that the attention is arrested at the outset.

The usual order of development of the subject is followed, but the treatment is by no means commonplace. In the discussion of a topic the author usually follows the order of the historical development of the subject, as being in most cases the natural approach. There is a notable exception to this, however, in the treatment of mechanics, where the usual method is followed, of beginning with motion and later taking up cases of equilibrium. It seems to us that in introducing *beginners* to so difficult a subject as mechanics, we would do well to follow the guidance of history and begin with questions of equilibrium before taking up problems involving acceleration with their attendant difficulties. Of course the method adopted has advantages when the object in view is the systematic presentation of the subject, and this is, doubtless, why it is so generally employed in spite of its disadvantages from a pedagogical standpoint.

The excellent plan has been adopted of giving the names of distinguished physicists in connection with their discoveries, and with each in brackets the dates of birth and death; thus almost unconsciously the student comes to have a historical perspective of the subject. The author's interest in the history of the subject leads him to reprint the very interesting original account of Boyle's experiments on the "Spring of the Air," and in the case of Torricelli's experiment to come to the defense of the old *horror vacui* theory in a way that is quite amusing.

A treatment of water waves that is unusually complete for an elementary text-book is an excellent feature. The change of front due to retardation in shoal water is discussed and used to advantage later in considering the refraction of light waves. It seems to us that in most of our text-books the subject of surface waves receives very scant treatment, considering its importance.

In treating the subject of electrical resistance the author prefers to approach it from the heating effect of the current, and does not take up Ohm's law till almost the last topic in his treatment of currents, though it would seem to us that the early introduction of the point of view of electric currents expressed by Ohm's law might be a help to the student.

Special references to other books are given at the ends of some of the chapters, with comments as to the character of the treatments referred to. These will doubtless be very helpful to a student wishing to go more extensively into some part of the subject.

The whole treatment, though elementary, is exact and quantitative, and numerous problems are given. The student who masters this text-book will have to *think*, but he will find himself stimulated and helped in his thinking by a natural presentation of the subject, by clear statements, lucid explanations and apt illustrations.

The general arrangement is clear and systematic, good use being made of different styles of type in emphasizing important points.

On the whole the book is to be distinctly approved as a freshly-written modern presentation of the subject, elementary, but exact and thorough, and well adapted for advanced high school instruction. The teacher will find in it many valuable suggestions. The author is a teacher of experience, who has evidently given thought to the art of presenting the subject so that it may be most readily grasped by the pupil.

ARTHUR L. KIMBALL.

A Text-book of Physics. By W. WATSON. London, Longmans, Green & Co., 1899. Pp. xxii + 896.

This addition to the rapidly growing list of physics text-books contains many notably commendable features. One recognizes in it at once the work of a skillful writer, an experienced teacher and a working physicist. Mr. Watson's volume is comprehensive in the sense that it states nearly every essential principle of physics, says something on all of the important phenomena, and describes a great number of the methods by which our knowledge of the leading facts of the science has been attained. There is likewise a wealth of well selected tabular data interspersed throughout the book. The volume is bulky, consisting of nearly 900 pages of closely printed matter, but when we turn to any given topic we find that its bulkiness is not due to the introduction of any considerable amount of detail in the description or in the theoretical discussions, but is simply a symbol of the enormous amount of material which has to be included in any treatise covering the domain of modern physics. The individual topics indeed are very briefly considered, and one is inclined to quarrel with them on the score of omission rather than because they are overloaded with unnecessary matter. The author's statements are for the most part clear, and in accordance with the accepted views of physicists.

One finds, as he must expect to find in any such treatise, minor points concerning which he would take issue; as, for example, where electromotive force and difference of potential are specifically stated to be different names for one and the same thing, or where, as in the diagram on page 516, wave-lengths of light are expressed in centimeters multipled by 10^{-10} (the minus sign in the exponent is omitted; a misprint that is not likely to mislead any one), instead of using, as elsewhere in the volume, one of the two accepted systems. It is true that the reference of wave-lengths to a unit thus simply related to the centimeter might well be preferred to either of those which have come into use, but it is a question whether in a text-book it is well to depart from the general practice, especially as the author in subsequent pages reverts to the beaten path.

These, however, are matters of little moment. The important thing is that Mr. Watson has produced for us a treatise on experimental physics, which contains brief and accurate statements of so many of the important topics in physics. The value of the book as a reference work would have been greatly increased by the introduction of citations of original sources, and this remark applies particularly to the well-selected tables of physical constants. Many of the illustrations are new, and some of them will be welcome additions to the store of illustrative material already at the command of the teacher.

We are glad to note what is really very unusual among British writers, even of the modern school: that is, a fairly consistent adherence to the gram, the centimeter and the second as fundamental units.

E. L. N.